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[Document Name] SPECIFICATION

[Title of the invention] RESIN PARTICLE AND METHOD FOR
PREPARING THE SAME

[Claims]

5 [Claim 1] A method for preparing resin particles, comprising
the steps of: applying a shear force to an aqueous dispersion
(II) with increased viscosity formed by adding a thickener (V)
to an aqueous dispersion (I) containing resin particles (A);
and a subsequent step of decreasing the viscosity of the aqueous
10 dispersion by adding a viscosity decreasing agent (E).

[Claim 2] The method according to claim 1, wherein the viscosity
of (II) is in the range of 300 to 100,000 mPa·s.

[Claim 3] The method according to claim 1 or 2, wherein the
viscosity of the aqueous dispersion after subjecting the
15 viscosity decreasing step is 200 mPa·s or less.

[Claim 4] The method according to any one of claims 1-3, wherein
(V) is water-soluble naturally-occurring polymers or
water-soluble semisynthetic polymers.

[Claim 5] The method according to any one of claims 1-4, wherein
20 (E) is α -glycanase and/or β -glycanase.

[Claim 6] The method according to any one of claims 1-5, wherein
(A) comprises at least one resin selected from the group
consisting of vinyl resins, polyurethanes, epoxy resins, and
polyesters.

25 [Claim 7] The method according to any one of claims 1-6, wherein
(I) is an aqueous dispersion obtained by reacting an active
group-containing prepolymer (α) with a curing agent (β) in an
aqueous medium.

[Claim 8] The method according to claim 7, wherein (α) has at
30 least one reactive group selected from the group consisting of
an isocyanate group, a blocked isocyanate group and an epoxy
group, and the (β) is an active hydrogen-containing compound

(β1).

[Claim 9] The method according to claim 8, wherein the (β1) is a ketimine compound and/or water.

5 [Claim 10] A resin particle (B) obtained in accordance with the method of any one of claims 1-9.

[Claim 11] The resin particle (B) according to claim 10, which has a shape factor (SF-1) of 110 to 180.

[Detailed description of the invention]

[0001]

10 [Technical field to which the invention belongs]

The present invention relates to a resin particle and method for preparation thereof. More particularly, the present invention relates to resin particles which can be of use as additives for paints, additives for coating materials, powder 15 coatings, additives for cosmetics, resins for slush molding, spacers for manufacturing electronic components or devices such as liquid crystal displays, standard particles for electronic measuring instruments, toners for electrophotography, electrostatic recording, or electrostatic printing, hot-melt 20 adhesives, other molding materials, and the like, and to method for preparing the same.

[0002]

[Prior art]

There are known resin particles prepared by a method in 25 which a resin solution, obtained by dissolving a resin in a solvent, is dispersed in an aqueous medium under the presence of a dispersing (assistant) agent such as a surfactant or a water-soluble polymer and then the solvent is removed by heating or decompression (that is, by a method of suspending a resin 30 solution in an aqueous medium: see Toku-Ko-Sho61-28688, Toku-Kai-Sho63-25664, Toku-Kai-Hei9-34167, for example).

[0003]

[Problems the invention intends to solve]

In general, as resin particles obtained by such a method of suspending a resin solution in an aqueous medium are spherical particles, such resin particles have a drawback that the fluidity 5 thereof tends to become excessive and the surface area thereof is small. Therefore, in a case where the resin particles are used as an additive for paint, obtained paint has a problem that the kinematic viscosity thereof is lowered, resulting in poor 10 coating properties. Further, in a case where the resin particles are used as a toner, there is a problem that cleaning of the toner with a cleaning blade is not satisfactorily carried out.

It is therefore an object of the present invention to provide a non-spherical (e.g., a spindle- or rod-shaped resin particle) resin particle with large surface area, and a method 15 for preparing such resin particles.

[0004]

[Means for solving the problems]

The present inventors have earnestly studied to solve the above-described problem, thereby leading to the present 20 invention. The present invention is a method for preparing resin particles, comprising the steps of applying a shear force to an aqueous dispersion (II) with increased viscosity formed by adding a thickener (V) to an aqueous dispersion (I) containing resin particles (A) and a subsequent step of decreasing the 25 viscosity of the aqueous dispersion by adding a viscosity decreasing agent (E), and resin particles (B) obtained by the preparing method according to the present invention.

[0005]

[Mode for carrying out the invention]

30 The ellipticity of the resin particles (B) obtained by the preparing method according to the present invention is expressed in terms of a shape factor (SF-1). The SF-1 of the

(B) is preferably in the range of 110 to 800, more preferably 110 to 500, still more preferably 120 to 500, even more preferably 120 to 400, especially preferably 120 to 300, especially more preferably 130 to 300, especially even more preferably 130 to 5 250, most preferably 130 to 200. That is, the upper limit of SF-1 is preferably 800, more preferably 500, still more preferably 400, even more preferably 300, still even more preferably 250, most preferably 200. The lower limit is preferably 110, more preferably 120, still more preferably 130. 10 By setting the SF-1 to a value within the above range, it is possible to obtain the following effects according to the purposes of use of the resin particles.

[0006]

Specifically, in a case where the resin particles are used 15 as an additive for paint or an additive for coating materials, such resin particles show significant thixotropy when dispersed in a solvent or an aqueous medium, and therefore the resin particles are particularly useful as a fluidity improving agent for paint and coating materials. Further, since the resin 20 particles are aligned uniformly in the direction of a longer diameter thereof in the formation of a coating, the effect of preventing blister from occurring in forming a coating and the effect of improving luster or a gloss of a coating can be obtained.

In this regard, it is to be noted that, in a case where 25 the resin particles are to be used as an additive for paint or an additive for coating materials, the SF-1 of the resin particles is preferably in the range of 110 to 800, more preferably 120 to 500, even more preferably 130 to 300. That is, in this case, the upper limit of SF-1 is preferably 800, more preferably 500, 30 even more preferably 300, the lower limit is preferably 110, more preferably 120, even more preferably 130.

[0007]

Further, in a case where the resin particles are used as an additive for cosmetics (e.g., lipstick and foundation), the resin particles facilitate smooth feeling when such cosmetics are applied to the skin. In a case where the resin particles 5 are used as a resin for slush molding or a hot-melt adhesive, powder fluidity and powder release properties at the time of application are improved.

In this regard, it is to be noted that, in a case where the resin particles are to be used as an additive for cosmetics 10 (e.g., lipstick and foundation), a resin for slush molding, or a hot-melt adhesive, the SF-1 of the resin particles is preferably in the range of 110 to 500, more preferably 120 to 300, even more preferably 130 to 200. That is, in this case, the upper limit of the SF-1 is preferably 500, more preferably 300, even 15 more preferably 200, the lower limit is preferably 110, more preferably 120, even more preferably 130.

[0008]

Furthermore, in a case where the resin particles are used as a toner for electrophotography, electrostatic recording or 20 electrostatic printing, cleaning of the toner with a cleaning blade is facilitated.

In this regard, it is to be noted that, in a case where the resin particles are to be used as a toner for electrophotography, electrostatic recording, or electrostatic 25 printing, the SF-1 of the resin particles is preferably in the range of 110 to 400, more preferably 120 to 300, even more preferably 130 to 250. That is, in this case, the upper limit of the SF-1 is preferably 400, more preferably 300, even more 30 preferably 250, the lower limit is preferably 110, more preferably 120, even more preferably 130.

[0009]

In the present invention, the shape factor (SF-1) is

determined by random sampling 100 images of the resin particles obtained by scaling up 500 times by the use of an electronic microscope (e.g., "FE-SEM (S-800)" which is manufactured by Hitachi, Ltd; the same applies to the following description),

5 inputting the image data into an image analyzer (e.g., "nexus NEW CUBE ver.2.5" manufactured by NEXUS Co., Ltd. and "Luzex III" manufactured by NIRECO Corporation; the same applies to the following description) via an interface to analyze the image data, and carrying out calculation using the formula (1).

10 [0010]

[Math.1]

$$(SF-1) = 100 \pi (MXLNG)^2 / 4 (AREA) \quad (1)$$

[wherein (MXLNG) represents the absolute longest length of the resin particle and (AREA) represents the projected area of the resin particle.]

15 [0011]

A resin particle (A) comprises a resin (a). The resin (a) may be either a thermoplastic resin or a thermosetting resin, and examples of the resin (a) include vinyl resins, polyurethanes, 20 epoxy resins, polyesters, polyamides, polyimides, silicone resins, phenolic resins, melamine resins, urea resins, aniline resins, ionomer resins, polycarbonates, and mixtures of two or more of them. Among them, from the viewpoint of obtaining uniform and fine spherical resin particles easily, vinyl resins, polyurethanes, epoxy resins, polyesters, and mixtures of two or more of them are preferred, vinyl resins, polyurethanes, polyesters, and mixtures of two or more of them are more preferred, and vinyl resins, polyesters, and mixtures of two or more of them are even more preferred.

25 [0012]

Hereinbelow, these resins to be preferably used as the resin (a), that is, vinyl resins, polyurethanes, epoxy resins,

and polyesters will be described, but the other resins mentioned above can also be used as the resin (a).

Vinyl resins are homopolymers or copolymers of vinyl monomers.

5 In polymerization, a well-known polymerization catalyst or the like can be used.

As vinyl monomers, the following compounds (1) to (10) can be used.

(1) Vinyl hydrocarbons:

10 (1-1) Aliphatic vinyl hydrocarbons:

alkenes having 2 to 12 carbon atoms (e.g., ethylene, propylene, butene, isobutylene, pentene, heptene, diisobutylene, octene, dodecene, octadecene, and α -olefins having 3 to 24 carbon atoms); and alkadienes having 4 to 12 carbon atoms (e.g., butadiene, 15 isoprene, 1,4-pentadiene, 1,6-hexadiene, and 1,7-octadiene).

[0013]

(1-2) Alicyclic vinyl hydrocarbons:

mono- or di-cycloalkenes having 6 to 15 carbon atoms (e.g., cyclohexene, vinylcyclohexene, and ethylidenebicycloheptene); 20 mono- or di-cycloalkadienes having 5 to 12 carbon atoms (e.g., (di)cyclopentadiene); terpenes (e.g., pinene, limonene, and indene); and the like.

[0014]

(1-3) Aromatic vinyl hydrocarbons:

25 styrene; hydrocarbyl(alkyl, cycloalkyl, aralkyl, and/or alkenyl each having 1 to 24 carbon atoms)-substituted styrene (e.g., α -methylstyrene, vinyltoluene, 2,4-dimethylstyrene, ethylstyrene, isopropylstyrene, butylstyrene, phenylstyrene, cyclohexylstyrene, benzylstyrene, crotylbenzene, 30 divinylbenzene, divinyltoluene, divinylxylene, and trivinylbenzene); vinylnaphthalene; and the like.

[0015]

(2) Carboxyl group-containing vinyl monomers and salts thereof:
unsaturated monocarboxylic acids having 3 to 30 carbon atoms
(e.g., (meth)acrylic acid, crotonic acid, isocrotonic acid and
cinnamic acid); unsaturated dicarboxylic acids

5 (anhydrides) having 3 to 30 carbon atoms (e.g., maleic acid
(anhydride), fumaric acid, itaconic acid, citraconic acid
(anhydride), and mesaconic acid); monoalkyl (having 1 to 24
carbon atoms) esters of unsaturated dicarboxylic acids having
3 to 30 carbon atoms (e.g., monomethyl ester of maleic acid,
10 monooctadecyl ester of maleic acid, monoethyl ester of fumaric
acid, monobutyl ester of itaconic acid, glycol monoether of
itaconic acid, and monoeicosyl ester of citraconic acid); and
the like.

[0016]

15 Examples of salts of the carboxyl group-containing vinyl
monomers include alkali metal salts (e.g., sodium salts and
potassium salts), alkaline-earth metal salts (e.g., calcium
salts and magnesium salts), ammonium salts, amine salts, and
quaternary ammonium salts. The amine salts are not limited to
20 any specific ones as long as they are amine compounds, but primary
amine salts (e.g., ethylamine salts, butylamine salts, and
octylamine salts), secondary amine salts (e.g., diethylamine
salts and dibutylamine salts), and tertiary amine salts (e.g.,
triethylamine salts and tributylamine salts) can be mentioned,
25 for example. As the quaternary ammonium salts,
tetraethylammonium salts, lauryltriethylammonium salts,
tetrabutylammonium salts, lauryltributylammonium salts, and
the like can be mentioned.

[0017]

30 Specific examples of salts of the carboxyl
group-containing vinyl monomers include sodium acrylate, sodium
methacrylate, monosodium maleate, disodium maleate, potassium

acrylate, potassium methacrylate, monopotassium maleate, lithium acrylate, cesium acrylate, ammonium acrylate, calcium acrylate, aluminum acrylate, and the like.

[0018]

5 (3) Sulfo group-containing vinyl monomers and salts thereof: alkenesulfonic acids having 2 to 14 carbon atoms (e.g., vinylsulfonic acid, (meth)allylsulfonic acid, and methylvinylsulfonic acid); styrenesulfonic acid and alkyl (having 2 to 24 carbon atoms) derivatives thereof (e.g.,

10 α -methylstyrenesulfonic acid); sulfo(hydroxy)alkyl-(meth)acrylates having 5 to 18 carbon atoms (e.g., sulfopropyl(meth)acrylate, 2-hydroxy-3-(meth)acryloxypropylsulfonic acid, 2-(meth)acryloyloxyethanesulfonic acid, and

15 3-(meth)acryloyloxy-2-hydroxypropanesulfoic acid); sulfo(hydroxy)alkyl(meth)acrylamides having 5 to 18 carbon atoms (e.g., 2-(meth)acryloylamino-2,2-dimethylethanesulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, and

20 3-(meth)acrylamide-2-hydroxypropanesulfonic acid); alkyl (having 3 to 18 carbon atoms) allylsulfosuccinic acids (e.g., propylallylsulfosuccinic acid, butylallylsulfosuccinic acid, and 2-ethylhexyl-allylsulfosuccinic acid); poly(n = 2 to 30)oxyalkylene(oxyethylene, oxypropylene, oxybutylene: homo, random, or block)mono(meth)acrylate sulfates (e.g., poly(n = 5 to 15)oxyethylene monomethacrylate sulfate and poly(n = 5 to 15)oxypropylene monomethacrylate sulfate); polyoxyethylene polycyclic phenyl ether sulfates (e.g., sulfates represented by the general formula (1-1) or (1-2)); sulfonic acids

25 represented by the general formula (1-3)); salts thereof; and the like.

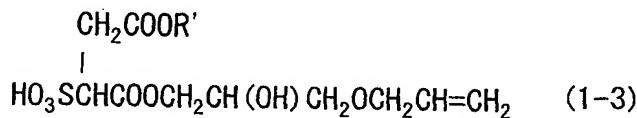
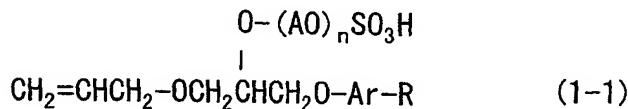
It is to be noted that counter ions mentioned with reference

to "(2) carboxyl group-containing vinyl monomers and salts thereof" or the like are used for the salts.

[0019]

[Chem.1]

5



10

[0020]

(wherein R represents an alkyl group having 1 to 15 carbon atoms, AO represents an oxyalkylene group having 2 to 4 carbon atoms, and wherein when n is plural, oxyalkylene groups may be 15 the same or different, and when different, they may be random, block and/or combination of random and block, Ar represents a benzen ring, n is an integer of 1 to 50, and R' represents an alkyl group having 1 to 15 carbon atoms which may be substituted by a fluorine atom.)

20 [0021]

(4) Phosphono group-containing vinyl monomers and salts thereof:

(meth)acryloyloxyalkyl (having 1 to 24 carbon atoms) monophosphates (e.g., 2-hydroxyethyl(meth)acryloyl phosphate 25 and phenyl-2-acryloyloxyethyl phosphate), and (meth)acryloyloxyalkyl(having 1 to 24 carbon atoms) phosphonic

acids (e.g., 2-acryloyloxyethylphosphonic acid).

[0022]

(5) Hydroxyl group-containing vinyl monomers:

hydroxystyrene, N-methylol(meth)acrylamide,

5 hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, polyethylene glycol mono(meth)acrylate, (meth)allyl alcohol, crotyl alcohol, isocrotyl alcohol, 1-butene-3-ol, 2-butene-1-ol, 2-butene-1,4-diol, propargyl alcohol, 2-hydroxyethyl propenyl ether, and allyl ether of sucrose, and
10 the like.

[0023]

(6) Nitrogen-containing vinyl monomers:

(6-1) Amino group-containing vinyl monomers:

aminoethyl (meth)acrylate, dimethylaminoethyl
15 (meth)acrylate, diethylaminoethyl (meth)acrylate, t-butyldiminoethyl methacrylate, N-aminoethyl (meth)acrylamide, (meth)allylamine, morpholinoethyl (meth)acrylate, 4-vinylpyridine, 2-vinylpyridine, crotylamine, N,N-dimethylaminostyrene, methyl α -acetaminoacrylate,
20 vinylimidazole, N-vinylpyrrole, N-vinylthiopyrrolidone, N-arylphenylenediamine, aminocarbazole, aminothiazole, aminoindole, aminopyrrole, aminoimidazole, aminomercaptothiazole, salts thereof, and the like.

[0024]

25 (6-2) Amide group-containing vinyl monomers:

(meth)acrylamide, N-methyl(meth)acrylamide,

N-butylacrylamide, diacetoneacrylamide,

N-methylol(meth)acrylamide,

N,N'-methylene-bis(meth)acrylamide, cinnamamide,

30 N,N-dimethylacrylamide, N,N-dibenzylacrylamide, methacryl formamide, N-methyl-N-vinylacetamide, and N-vinylpyrrolidone, and the like.

[0025]

(6-3) Nitrile group-containing vinyl monomers having 3 to 10 carbon atoms:

5 (meth)acrylonitrile, cyanostyrene, cyanoacrylate, and the like.

(6-4) Quaternary ammonium cation group-containing vinyl monomers:

10 quaternization products (obtained using a quaternizing agent such as methyl chloride, dimethyl sulfate, benzyl chloride, dimethyl carbonate or the like) of tertiary amine group-containing vinyl monomers such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, diallylamine, and the like 15 (e.g., dimethyldiallylammonium chloride and trimethylallylammonium chloride).

(6-5) Nitro group-containing vinyl monomers having 8 to 12 carbon atoms:

nitrostyrene and the like.

20 [0026]

(7) Epoxy group-containing vinyl monomers having 6 to 18 carbon atoms:

glycidyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, p-vinylphenyl oxide, and the like.

25 (8) Halogen-containing vinyl monomers having 2 to 16 carbon atoms:

vinyl chloride, vinyl bromide, vinylidene chloride, allyl chloride, chlorostyrene, bromostyrene, dichlorostyrene, chloromethylstyrene, tetrafluorostyrene, chloroprene, and the like.

30 [0027]

(9) Vinyl esters, vinyl (thio)ethers, vinyl ketones, and vinyl

sulfones:

(9-1) vinyl esters having 4 to 16 carbon atoms:

for example, vinyl acetate, vinyl butyrate, vinyl propionate, vinyl butyrate, diallyl phthalate, diallyl adipate, isopropenyl 5 acetate, vinyl methacrylate, methyl 4-vinylbenzoate, cyclohexyl methacrylate, benzyl methacrylate, phenyl (meth)acrylate, vinyl methoxyacetate, vinyl benzoate, ethyl α -ethoxyacrylate, alkyl (meth)acrylates having an alkyl group containing 1 to 50 carbon atoms (e.g., methyl (meth)acrylate, 10 ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate, hexadecyl (meth)acrylate, heptadecyl (meth)acrylate, and eicosyl (meth)acrylate), dialkyl fumarates (whose two alkyl groups are straight, branched or alicyclic 15 groups having 2 to 8 carbon atoms), dialkyl maleates (whose two alkyl groups are straight, branched or alicyclic groups having 2 to 8 carbon atoms), poly(meth)allyloxyalkanes (e.g., diallyloxyethane, triallyloxyethane, tetraallyloxyethane, tetraallyloxypropane, tetraallyloxybutane, and 20 tetramethallyloxyethane), vinyl-based monomers having a polyalkylene glycol chain [e.g., polyethylene glycol (molecular weight: 300) mono(meth)acrylate, polypropylene glycol (molecular weight: 500) monoacrylate, methyl alcohol-ethylene oxide (10 mol) adduct (meth)acrylate, and lauryl 25 alcohol-ethylene oxide (30 mol) adduct (meth)acrylate], and poly(meth)acrylates (e.g., poly(meth)acrylates of polyhydric alcohols: ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, and polyethylene glycol 30 di(meth)acrylate), and the like.

[0028]

(9-2) Vinyl (thio)ethers having 3 to 16 carbon atoms:

vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, vinyl butyl ether, vinyl 2-ethylhexyl ether, vinyl phenyl ether, vinyl 2-methoxyethyl ether, methoxybutadiene, vinyl 2-butoxyethyl ether, 3,4-dihydro-1,2-pyran,

5 2-butoxy-2'-vinyloxydiethylether, vinyl 2-ethylmercaptoethyl ether, acetoxystyrene, and phenoxystyrene, and the like.

[0029]

(9-3) Vinyl ketones having 4 to 12 carbon atoms (e.g., vinyl methyl ketone, vinyl ethyl ketone, and vinyl phenyl ketone),

10 vinyl sulfones having 2 to 16 carbon atoms (e.g., divinyl sulfide, p-vinyl diphenyl sulfide, vinyl ethyl sulfide, vinyl ethyl sulfone, divinyl sulfone, and divinyl sulfoxide), and the like.

[0030]

(10) Other vinyl monomers:

15 isocyanatoethyl (meth)acrylate, m-isopropenyl- α , α -dimethylbenzyl isocyanate, and the like.

Among these vinyl monomers, vinyl hydrocarbons, carboxyl group-containing vinyl monomers and salts thereof, sulfonic acid group-containing vinyl monomers and salts thereof, hydroxyl group-containing vinyl monomers, and nitrogen-containing vinyl monomers are preferably used, more preferably, vinyl hydrocarbons, carboxyl group-containing vinyl monomers and salts thereof, and sulfonic acid group-containing vinyl monomers and salts thereof, even more preferably aromatic vinyl-based hydrocarbons, carboxyl group-containing vinyl monomers and salts thereof, and sulfonic acid group-containing vinyl monomers and salts thereof.

[0031]

Among vinyl resins, as polymers obtained by copolymerizing vinyl monomers (copolymers of vinyl monomers), polymers obtained by copolymerizing two or more of the monomers mentioned in (1) to (10) in any ratio are used. Examples of such copolymers

include styrene-(meth)acrylate copolymer, styrene-butadiene copolymer, (meth)acrylic acid-(meth)acrylate copolymer, styrene-acrylonitrile copolymer, styrene-maleic acid (anhydride) copolymer, styrene-(meth)acrylic acid copolymer, 5 styrene-(meth)acrylic acid-divinylbenzene copolymer, and styrene-styrenesulfonic acid-(meth)acrylate copolymer, and the like.

[0032]

As polyesters, polycondensation products of polyols with 10 polycarboxylic acids, acid anhydrides thereof or lower alkyl esters thereof (alkyl groups having 1 to 4 carbon atoms), and the like can be used.

In polycondensation reaction, a well-known polycondensation catalyst or the like can be used.

15 As polyols, diols (11) and polyols (12) having 3 to 6 or more hydroxyl groups can be used.

As polycarboxylic acids, acid anhydrides thereof, and lower alkyl esters thereof, dicarboxylic acids (13), polycarboxylic acids (14) having 3 to 4 or more carboxyl groups, 20 acid anhydrides thereof, and lower alkyl esters thereof can be used.

[0033]

Examples of the diols (11) include alkylene glycols having 4 to 30 carbon atoms (e.g., ethylene glycol, 1,2-propylene glycol, 25 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, octanediol, decanediol, dodecanediol, tetradecanediol, neopentyl glycol, and 2,2-diethyl-1,3-propanediol), alkylene ether glycols having a molecular weight of 50 to 10,000 (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, 30 polyethylene glycol, polypropylene glycol, and polytetramethylene ether glycol), alicyclic diols having 6 to 24 carbon atoms (e.g., 1,4-cyclohexane dimethanol and

hydrogenated bisphenol A), bisphenols having 15 to 30 carbon atoms (e.g., bisphenol A, bisphenol F, and bisphenol S), polyphenols having 12 to 24 carbon atoms (e.g., catechol, hydroquinone, and resorcin), alkylene oxides [e.g., ethylene 5 oxide, propylene oxide, and butylene oxide] (2 to 100 mol) adducts of the above-mentioned alicyclic diols having a molecular weight of 100 to 10,000 (e.g., ethylene oxide (10 mol) adduct of 1,4-cyclohexane dimethanol), alkylene oxide (ethylene oxide, 10 propylene oxide, or butylene oxide) (2 to 100 mol) adducts of the above-mentioned bisphenols (e.g., ethylene oxide (2 mol) 15 adduct of bisphenol A, ethylene oxide (4 mol) adduct of bisphenol A, propylene oxide (2 mol) adduct of bisphenol A, propylene oxide (3 mol) adduct of bisphenol A, and propylene oxide (4 mol) adduct of bisphenol A), polylactonediols having a weight average molecular weight of 100 to 5,000 (e.g., poly- ϵ -caprolactonediol), polybutadienediol having a weight average molecular weight of 1,000 to 20,000, and the like.

Among these diols, alkylene glycols and alkylene oxide adducts of bisphenols are preferably used, more preferably 20 alkylene oxide adducts of bisphenols and mixtures of alkylene oxide adducts of bisphenols and alkylene glycols.

[0034]

Examples of the polyols (12) having 3 to 6 or more hydroxyl groups include tri- to octa- or more polyhydric aliphatic 25 alcohols having 3 to 8 carbon atoms (e.g., glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitan, and sorbitol), trisphenols having 25 to 50 carbon atoms (e.g., trisphenol PA), novolac resins having a degree of polymerization of 3 to 50 (e.g., phenol novolac and cresol 30 novolac), polyphenols having 6 to 30 carbon atoms (e.g., pyrogallol, phloroglucinol, and 1,2,4-benzenetriol), alkylene (having 2 to 4 carbon atoms) oxide (2 to 100 mol) adducts of

the trisphenols mentioned above (e.g., ethylene oxide (2 mol) adduct of trisphenol PA, ethylene oxide (4 mol) adduct of trisphenol PA, propylene oxide (2 mol) adduct of trisphenol PA, propylene oxide (3 mol) adduct of trisphenol A, and propylene oxide (4 mol) adduct of trisphenol PA), alkylene (having 2 to 4 carbon atoms) oxide (2 to 100 mol) adducts of the novolac resins mentioned above (e.g., propylene oxide (2 mol) adduct of phenol novolac and ethylene oxide (4 mol) adduct of phenol novolac), alkylene (having 2 to 4 carbon atoms) oxide (2 to 100 mol) adducts 10 of the polyphenols mentioned above (e.g., ethylene oxide (4 mol) adduct of pyrogallol), and acrylic polyols having a degree of polymerization of 20 to 2,000 (e.g., copolymers of hydroxyethyl (meth)acrylate with other vinyl monomers such as styrene, (meth)acrylic acid, and (meth)acrylate), and the like.

15 Among these polyols, polyhydric aliphatic alcohols and alkylene oxide adducts of novolac resins are preferably used, more preferably alkylene oxide adducts of novolac resins.

[0035]

Examples of the dicarboxylic acids (13) include 20 alkanedicarboxylic acids having 4 to 32 carbon atoms (e.g., succinic acid, adipic acid, sebacic acid, dodeceny succinic acid, azelaic acid, dodecanedicarboxylic acid, and octadecanedicarboxylic acid), alkenedicarboxylic acids having 4 to 32 carbon atoms (e.g., maleic acid, fumaric acid, citraconic acid, and mesaconic acid), branched-chain alkenedicarboxylic acids having 8 to 40 carbon atoms (e.g., dimer acid and alkenylsuccinic acids such as dodeceny succinic acid, pentadeceny succinic acid, and octadeceny succinic acid), 25 branched-chain alkanedicarboxylic acids having 12 to 40 carbon atoms (e.g., alkylsuccinic acids such as decylsuccinic acid, dodecylsuccinic acid, and octadecylsuccinic acid), and aromatic dicarboxylic acids having 8 to 20 carbon atoms (e.g., phthalic

acid, isophthalic acid, terephthalic acid, and naphthalenedicarboxylic acid), and the like.

Among these dicarboxylic acids (13), alkenedicarboxylic acids and aromatic dicarboxylic acids are preferably used, more 5 preferably aromatic dicarboxylic acids.

[0036]

Examples of the polycarboxylic acids (14) having 3 to 4 or more carboxyl groups include aromatic polycarboxylic acids having 9 to 20 carbon atoms, such as trimellitic acid, and 10 pyromellitic acid, and the like.

Examples of acid anhydrides of the dicarboxylic acids (13) and the polycarboxylic acids (14) having 3 to 4 or more carboxyl groups include trimellitic anhydride and pyromellitic anhydride. Or, examples of lower alkyl esters thereof include methyl esters, 15 ethyl esters, and isopropyl esters.

[0037]

In forming the polyester to be used in the present invention, the diols, the polyols having 3 to 6 or more hydroxyl groups, the dicarboxylic acids, the polycarboxylic acids having 3 to 20 4 or more carboxyl groups, and mixtures of two or more of them can be used in any ratio. The equivalent ratio of hydroxyl group [OH] to carboxyl group [COOH], that is, [OH]/[COOH] is preferably in the range of 2/1 to 1/1, more preferably in the range of 1.5/1 to 1/1, even more preferably in the range of 1.3/1 to 1.02/1. 25 That is, the upper limit of the equivalent ratio [OH]/[COOH] is preferably 2/1, more preferably 1.5/1, even more preferably 1.3/1, the lower limit is preferably 1/1, even more preferably 1.02/1.

Further, the ester equivalent (that is, a molecular weight 30 per one equivalent of ester group) in the polyester is preferably in the range of 50 to 2,000, more preferably in the range of 60 to 1,000, even more preferably in the range of 70 to 500.

That is, the upper limit of the ester equivalent in the polyester is preferably 2000, more preferably 1000, even more preferably 500, the lower limit is preferably 50, more preferably 60, even more preferably 70.

5 [0038]

As polyurethanes, polyaddition products of polyisocyanates (15) and active hydrogen-containing compounds ($\beta 1$) (e.g., water, the diols (11), the polyols (12) having 3 to 6 or more hydroxyl groups, the dicarboxylic acids (13), the 10 polycarboxylic acids (14) having 3 to 4 or more carboxyl groups, polyamines (16), and polythiols (17)), and the like can be used.

In polyaddition reaction, a well-known polyaddition reaction catalyst or the like can be used.

[0039]

15 Examples of the polyisocyanates (15) include aromatic polyisocyanates having 6 to 20 carbon atoms (exclusive of the carbon in an NCO group; the same applies to the following description), aliphatic polyisocyanates having 2 to 18 carbon atoms, alicyclic polyisocyanates having 4 to 15 carbon atoms, 20 araliphatic polyisocyanates having 8 to 15 carbon atoms, and modification products of these polyisocyanates (e.g., modified polyisocyanates having urethane, carbodiimide, allophanate, urea, biuret, urethodione, urethoimine, isocyanurate, or oxazolidone groups), mixtures of two or more of them, and the 25 like.

[0040]

Examples of the aromatic polyisocyanates include 1,3- or 1,4-phenylene diisocyanate, 2,4- or 2,6-tolylene diisocyanate (TDI), crude TDI, 2,4'- or 4,4'-diphenylmethane diisocyanate 30 (MDI), crude MDI [phosgenide of crude diaminophenylmethane [a condensation product of formaldehyde with aromatic amine (aniline) or a mixture containing such aromatic amine; a mixture

of diaminodiphenylmethane and a small amount (e.g., 5 to 20 %) of polyamine having 3 or more amino groups]: polyallyl polyisocyanate (PAPI)], 1,5-naphthylene diisocyanate,

4,4',4''-triphenylmethane triisocyanate, m- or

5 p-isocyanatophenylsulfonyl isocyanate, mixtures of two or more of them, and the like.

[0041]

Examples of the aliphatic polyisocyanates include ethylene diisocyanate, tetramethylene diisocyanate,

10 hexamethylene diisocyanate (HDI), dodecamethylene diisocyanate, 1,6,11-undecane triisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, lysine diisocyanate, 2,6-diisocyanatomethyl caproate, bis(2-isocyanatoethyl) fumarate, bis(2-isocyanatoethyl) carbonate,

15 2-isocyanatoethyl-2,6-diisocyanatohexanoate, mixtures of two or more of them, and the like.

[0042]

Examples of the alicyclic polyisocyanates include isophorone diisocyanate (IPDI),

20 dicyclohexylmethane-4,4'-diisocyanate (hydrogenated MDI), cyclohexylene diisocyanate, methylcyclohexylene diisocyanate (hydrogenated TDI),

bis(2-isocyanatoethyl)-4-cyclohexene-1,2-dicarboxylate, 2,5- or 2,6-norbornane diisocyanate, mixtures of two or more 25 of them, and the like.

[0043]

Examples of the araliphatic polyisocyanates include m- or p-xylylene diisocyanate (XDI),

30 $\alpha, \alpha, \alpha', \alpha'$ -tetramethylxylylene diisocyanate (TMXDI), mixtures of two or more of them, and the like.

Examples of the modification products of polyisocyanates include modified polyisocyanates having urethane, carbodiimide,

allophanate, urea, biuret, urethodione, urethoimine, isocyanurate and/or oxazolidone groups, such as modified MDI (e.g., urethane-modified MDI, carbodiimide-modified MDI, and trihydrocarbyl phosphate-modifiedMDI), urethane-modifiedTDI, 5 mixtures of two or more of them [e.g., a mixture of the modified MDI and the urethane-modified TDI (isocyanate-containing prepolymer)], and the like.

Among these polyisocyanates, aromatic polyisocyanates, aliphatic polyisocyanates, and alicyclic polyisocyanates are 10 preferably used, more preferably TDI, MDI, HDI, hydrogenated MDI, and IPDI.

[0044]

As polyamines (16), aliphatic polyamines having 2 to 18 carbon atoms, aromatic polyamines having 6 to 20 carbon atoms, 15 and the like can be used.

As aliphatic polyamines having 2 to 18 carbon atoms, (1) aliphatic polyamines, (2) alkyl (having 1 to 4 carbon atoms)-or hydroxyalkyl (having 2 to 4 carbon atoms)-substituted aliphatic polyamines mentioned above, (3) alicyclic or 20 heterocycle-containing aliphatic polyamines, (4) aromatic ring-containing aliphatic amines having 8 to 15 carbon atoms, and the like can be used.

[0045]

(1) Examples of the aliphatic polyamines include 25 alkylendiamines having 2 to 12 carbon atoms (e.g., ethylenediamine, propylenediamine, trimethylenediamine, tetramethylenediamine, and hexamethylenediamine), polyalkylene (having 2 to 6 carbon atoms) polyamines [e.g., diethylenetriamine, iminobispropylamine, 30 bis(hexamethylene)triamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine], and the like.

[0046]

(2) Examples of the alkyl (having 1 to 4 carbon atoms)-or hydroxyalkyl (having 2 to 4 carbon atoms)-substituted aliphatic polyamines mentioned above include dialkyl (having 1 to 3 carbon atoms) aminopropylamine, trimethylhexamethylenediamine, aminoethylmethanolamine, 2,5-dimethyl-2,5-hexamethylenediamine, and methyliminobispropylamine, and the like.

[0047]

(3) Examples of the alicyclic or heterocycle-containing aliphatic polyamines include alicyclic polyamines having 4 to 15 carbon atoms {e.g., 1,3-diaminocyclohexane, isophoronediamine, menthenediamine, 4,4'-methylenedicyclohexanediamine (hydrogenated methylenedianiline), and 3,9-bis(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5,5]undecane}, and heterocyclic polyamines having 4 to 15 carbon atoms [e.g., piperazine, N-aminoethylpiperazine, 1,4-diaminoethylpiperazine, and 1,4-bis(2-amino-2-methylpropyl)piperazine], and the like.

(4) Examples of the aromatic ring-containing aliphatic amines (having 8 to 15 carbon atoms) include xylylenediamine, tetrachloro-p-xylylenediamine, and the like.

[0048]

As the above-mentioned aromatic polyamines having 6 to 20 carbon atoms, (1) unsubstituted aromatic polyamines, (2) aromatic polyamines nuclearly substituted by one or more alkyl groups (having 1 to 4 carbon atoms, such as methyl, ethyl, n- or i-propyl and butyl), (3) aromatic polyamines having one or more electron-attracting groups such as halogen (e.g., Cl, Br, I, and F), alkoxy groups (e.g., methoxy and ethoxy), and a nitro group as nuclear substituents, and (4) secondary amino

group-containing aromatic polyamines, and the like can be used.

[0049]

(1) Examples of the unsubstituted aromatic polyamines include 1,2-, 1,3- or 1,4-phenylenediamine, 2,4'- or 5 4,4'-diphenylmethanedianamine, crude diphenylmethanedianamine (polyphenylpolymethylenepolyamine), diaminodiphenyl sulfone, benzidine, thiodianiline, bis(3,4-diaminophenyl) sulfone, 10 2,6-diaminopyridine, m-aminobenzylamine, triphenylmethane-4,4',4''-triamine, naphthylenediamine, mixtures of two or more of them, and the like.

[0050]

(2) Examples of the aromatic polyamines nuclearly substituted by one or more alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl, n- or i-propyl and butyl include 15 2,4- or 2,6-tolylenediamine, crude tolylenediamine, diethyltolylenediamine, 4,4'-diamino-3,3'-dimethyldiphenylmethane, 4,4'-bis(o-toluidine), dianisidine, diaminoditolyl sulfone, 1,3-dimethyl-2,4-diaminobenzene, 20 1,3-diethyl-2,4-diaminobenzene, 1,3-dimethyl-2,6-diaminobenzene, 1,4-diethyl-2,5-diaminobenzene, 1,4-diisopropyl-2,5-diaminobenzene, 1,4-dibutyl-2,5-diaminobenzene, 2,4-diaminomesitylene, 25 1,3,5-triethyl-2,4-diaminobenzene, 1,3,5-triisopropyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene, 2,3-dimethyl-1,4-diaminonaphthalene, 30 2,6-dimethyl-1,5-diaminonaphthalene, 2,6-diisopropyl-1,5-diaminonaphthalene, 2,6-dibutyl-1,5-diaminonaphthalene,

3,3',5,5'-tetramethylbenzidine,
3,3',5,5'-tetraisopropylbenzidine,
3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane,
3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane,
5 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane,
3,3',5,5'-tetrabutyl-4,4'-diaminodiphenylmethane,
3,5-diethyl-3'-methyl-2',4-diaminodiphenylmethane,
3,5-diisopropyl-3'-methyl-2',4-diaminodiphenylmethane,
3,3'-diethyl-2,2'-diaminodiphenylmethane,
10 4,4'-diamino-3,3'-dimethyldiphenylmethane,
3,3',5,5'-tetraethyl-4,4'-diaminobenzophenone,
3,3',5,5'-tetraisopropyl-4,4'-diaminobenzophenone,
3,3',5,5'-tetraethyl-4,4'-diaminodiphenyl ether,
3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenyl sulfone,
15 mixtures of two or more of them, and the like.

[0051]

(3) Examples of the aromatic polyamines having one or more electron-attracting groups (such as halogen e.g., a chlorine atom, a bromine atom, an iodine atom, and a fluorine atom; alkoxy groups e.g., methoxy and ethoxy; and a nitro group) as nuclear substituents include methylenebis-o-chloroaniline,
20 4-chloro-o-phenylenediamine, 2-chloro-1,4-phenylenediamine,
3-amino-4-chloroaniline, 4-bromo-1,3-phenylenediamine,
2,5-dichloro-1,4-phenylenediamine,
25 5-nitro-1,3-phenylenediamine, 3-dimethoxy-4-aminoaniline,
4,4'-diamino-3,3'-dimethyl-5,5'-dibromo-diphenylmethane,
3,3'-dichlorobenzidine, 3,3'-dimethoxybenzidine,
bis(4-amino-3-chlorophenyl)oxide,
bis(4-amino-2-chlorophenyl)propane,
30 bis(4-amino-2-chlorophenyl)sulfone,
bis(4-amino-3-methoxyphenyl)decane,
bis(4-aminophenyl)sulfide, bis(4-aminophenyl)telluride,

bis(4-aminophenyl)selenide,
bis(4-amino-3-methoxyphenyl)disulfide,
4,4'-methylenebis(2-iodoaniline),
4,4'-methylenebis(2-bromoaniline),
5 4,4'-methylenebis(2-fluoroaniline),
4-aminophenyl-2-chloroaniline, and the like.

[0052]

(4) Examples of the secondary amino group-containing aromatic polyamines include: aromatic polyamines obtained by 10 replacing some or all of -NH₂ groups in the aromatic polyamines (1) to (3) with -NH-R' groups (wherein R' represents an alkyl group such as a lower alkyl group having 1 to 4 carbon atoms e.g., methyl, ethyl, or the like), such as
4,4'-di(methylamino)diphenylmethane, and
15 1-methyl-2-methylamino-4-aminobenzene, and the like; polyamide polyamines such as low molecular-weight polyamide polyamines obtained by condensation of dicarboxylic acids (e.g., dimer acid) with excess (that is, 2 or more mols per mol of the acid) polyamines (e.g., the alkylene diamines and the polyalkylene polyamines 20 mentioned above); polyether polyamines such as hydrides of cyanoethylation products of polyether polyols (e.g., polyalkylene glycol); and the like.

[0053]

As polythiols (17), dithiols having 2 to 24 carbon atoms, 25 tri- to hexa- or higher valent polythiols having 5 to 30 carbon atoms, and the like can be used.

Examples of dithiols include ethylenedithiol, 1,4-butanedithiol, 1,6-hexanedithiol, and the like.

Examples of polythiols include Capcure-3800 30 (manufactured by Japan Epoxy Resins Co., Ltd.), polyvinylthiol, and the like.

[0054]

Among these active hydrogen-containing compounds (β 1), water, the diols (11), the polyols (12), the dicarboxylic acids (13), and the polyamines (16) are preferably used, more preferably water, the diols (11), the polyols (12), and the polyamines (16), even more preferably the diols (11), the polyols (12), and the polyamines (16).

5 [0055]

As epoxy resins, ring-opening polymerization products of polyepoxides (18), polyaddition products of the polyepoxides 10 (18) and the active hydrogen-containing compounds (β 1), and curing reaction products of the polyepoxides (18) and acid anhydrides of the dicarboxylic acids (13) or the polycarboxylic acids (14) having 3 to 4 or more carboxyl groups, and the like can be used.

15 In ring-opening polymerization reaction, polyaddition reaction, and curing reaction, a well-known catalyst or the like can be used.

15 [0056]

The polyepoxide (18) is not limited to any specific one 20 as long as it has two or more epoxy groups in the molecule, but from the viewpoint of mechanical characteristics of the cured product, it preferably has 2 to 6 epoxy groups in the molecule.

The epoxy equivalent (that is, molecular weight per epoxy group) of the polyepoxide (18) is preferably in the range of 25 65 to 1,000, more preferably 70 to 500, even more preferably 90 to 300. That is, the upper limit of the epoxy equivalent is preferably 1000, more preferably 500, even more preferably 300, the lower limit is preferably 65, more preferably 70, even more preferably 90. If the epoxy equivalent exceeds the above 30 upper limit, the cross-linked structure tends to be loose, thus resulting in lowering of physical properties of the cured product, such as water resistance, chemical resistance, mechanical

strength, and the like. On the other hand, it is difficult to get (or synthesize) polyepoxides having an epoxy equivalent less than the above lower limit.

[0057]

5 As polyepoxides (18), aromatic polyepoxides, heterocycle-containing polyepoxides, alicyclic polyepoxides, aliphatic polyepoxides, and the like can be used.

As aromatic polyepoxides, glycidyl ethers of polyhydric phenols, glycidyl esters of polyhydric phenols, glycidyl 10 aromatic polyamines, and glycidylation products of aminophenols, and the like can be used.

[0058]

Examples of the glycidyl ethers of polyhydric phenols include bisphenol F diglycidyl ether, bisphenol A diglycidyl 15 ether, bisphenol B diglycidyl ether, bisphenol AD diglycidyl ether, bisphenol S diglycidyl ether, bisphenol A diglycidyl halides, tetrachlorobisphenol A diglycidyl ether, catechin diglycidyl ether, resorcinol diglycidyl ether, hydroquinone diglycidyl ether, pyrogallol triglycidyl ether, 20 1,5-dihydroxynaphthalene diglycidyl ether, dihydroxybiphenyl diglycidyl ether, octachloro-4,4'-dihydroxybiphenyl diglycidyl ether, tetramethylbiphenyl diglycidyl ether, dihydroxynaphthylcresol triglycidyl ether, tris(hydroxyphenyl)methane triglycidyl ether, dinaphthyltriol 25 triglycidyl ether, tetrakis(4-hydroxyphenyl)ethane tetraglycidyl ether, p-glycidylphenyldimethyltolyl bisphenol A glycidyl ether, trimethyl-tert-butyl-butylhydroxymethane triglycidyl ether, 9,9'-bis(4-hydroxyphenyl)fluorene diglycidyl ether, 4,4'-oxybis(1,4-phenylethyl)tetraresol 30 glycidyl ether, 4,4'-oxybis(1,4-phenylethyl)phenyl glycidyl ether, bis(dihydroxynaphthalene) tetraglycidylether, glycidyl ether of phenol or cresol novolac resin, glycidyl ether of

limonene phenol novolac resin, diglycidyl ether obtained by the reaction between 2 mols of bisphenol A and 3 mols of epichlorohydrin, polyglycidyl ethers of polyphenols obtained by condensation reaction of phenol with glyoxal, glutaraldehyde, 5 or formaldehyde, polyglycidyl ether of polyphenol obtained by condensation reaction of resorcin with acetone, and the like.

[0059]

Examples of the glycidyl esters of polyhydric phenols include diglycidyl phthalate, diglycidyl isophthalate, 10 diglycidyl terephthalate, and the like.

Examples of the glycidyl aromatic polyamines include N,N-diglycidylaniline, N,N,N',N'-tetraglycidylxylylenediamine, and N,N,N',N'-tetraglycidylidiphenylmethanediamine, and the like.

15 Further, the epoxides include: triglycidyl ether of p-aminophenol; diglycidyl urethane compounds obtained by the addition reaction of tolylene diisocyanate or diphenylmethane diisocyanate and glycidol; and diglycidyl ethers of alkylene oxide (ethylene oxide or propylene oxide) (2 to 20 mol) adducts 20 of bisphenol A (e.g., diglycidyl ether of EO (4 mol) adduct of bisphenol A).

[0060]

As heterocyclic polyepoxides, trisglycidylmelamine can be used.

25 As alicyclic polyepoxides, vinylcyclohexene dioxide, limonene dioxide, dicyclopentadiene dioxide, bis(2,3-epoxycyclopentyl) ether, ethylene glycol bisepoxydicyclopentyl ether, 3,4-epoxy-6-methylcyclohexylmethyl-3',4'-epoxy-6'-methylcyc 30 lohexanecarboxylate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl)butylamine, dimer

acid diglycidyl ester, and nuclear hydrogenation products of aromatic polyepoxides (e.g., hydrogenated bisphenol F diglycidyl ether and hydrogenated bisphenol A diglycidyl ether) can be used, for example.

5 [0061]

As aliphatic polyepoxides, polyglycidyl ethers of polyhydric aliphatic alcohols, polyglycidyl esters of polyvalent fatty acids, glycidyl aliphatic amines, and the like can be used.

10 Examples of the polyglycidyl ethers of polyhydric aliphatic alcohols include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, tetramethylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol 15 diglycidyl ether, polytetramethylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, trimethylolpropane polyglycidyl ether, glycerol polyglycidyl ether, pentaerythritol polyglycidyl ether, sorbitol polyglycidyl ether, polyglycerol polyglycidyl ether, and the like.

20 [0062]

Examples of the polyglycidyl esters of polyvalent fatty acids include diglycidyl oxalate, diglycidyl maleate, diglycidyl succinate, diglycidyl glutarate, diglycidyl adipate, diglycidyl pimelate, and the like.

25 Examples of the glycidyl aliphatic amines include N,N,N',N'-tetraglycidyl hexamethylenediamine, and N,N,N',N'-tetraglycidyl ethylenediamine, and the like.

The aliphatic polyepoxides include (co)polymers of diglycidyl ethers and glycidyl(meth)acrylates.

30 Among these polyepoxides, aliphatic polyepoxy compounds and aromatic polyepoxy compounds are preferably used. In the present invention, the polyepoxides may be used in combination

of two or more of them.

[0063]

The resin (a) constitutes a resin particle (B). The number average molecular weight (Mn), Tg, melting point, and SP value 5 of the resin (a) can be appropriately adjusted to a value within a preferred range according to the purpose of use of the resin particles (B).

For example, in a case where the resin particles (B) are to be used as a resin for slush molding or a powder coating material, 10 the Mn of the resin (a) is preferably in the range of 2,000 to 500,000, more preferably in the range of 2,500 to 200,000, even more preferably in the range of 4,000 to 100,000.

In this regard, it should be noted that the number average molecular weights (Mn) and weight average molecular weights (Mw) 15 in this specification were measured by gel permeation chromatography (GPC) (using a THF solvent and polystyrene as a standard substance).

Further, in a case where the resin (a) has a melting point, the melting point of the resin (a) is preferably in the range 20 of 0 to 250°C, more preferably in the range of 35 to 200°C, even more preferably in the range of 40 to 180°C.

In this regard, it should be noted that the melting points in this specification were measured by DSC (at a temperature rising rate of 20°C/min).

25 [0064]

Furthermore, the Tg of the resin (a) is preferably in the range of -60 to 100°C, more preferably in the range of -40 to 80°C, even more preferably in the range of -30 to 70°C.

In this regard, it should be noted that the values of Tg 30 in this specification were determined by DSC (differential scanning calorimeter, at a temperature rising rate of 20°C/min).

Moreover, the SP value of the resin (a) is preferably in

the range of 7 to 18, more preferably in the range of 8 to 16, even more preferably in the range of 9 to 14.

In this regard, it should be noted that the SP values were calculated according to a method described in *Polymer Engineering and Science*, February 1974, Vol. 14, No. 2, pp. 147 to 154.
5 [0065]

In a case where the resin particles (B) are to be used as a spacer for use in manufacturing electronic components or devices such as liquid crystal displays or as standard particles 10 for electronic measuring instruments, the Mn of the resin (a) is preferably in the range of 10,000 to 10,000,000, more preferably in the range of 15,000 to 2,000,000, even more preferably in the range of 20,000 to 1,000,000.

Further, in a case where the resin (a) has a melting point, 15 the melting point of the resin (a) is preferably in the range of 50 to 300°C, more preferably in the range of 80 to 250°C, even more preferably in the range of 100 to 240°C.

25 [0066]

Furthermore, the Tg of the resin (a) is preferably in the 20 range of 0 to 250°C, more preferably in the range of 20 to 200°C, even more preferably in the range of 35 to 150°C.

Moreover, the SP value of the resin (a) is preferably in the range of 8 to 18, more preferably in the range of 9 to 16, even more preferably in the range of 9.5 to 14.

25 [0067]

In a case where the resin particles (B) are to be used as a toner for electrophotography, electrostatic recording, or electrostatic printing, the Mn of the resin (a) is preferably in the range of 1,000 to 5,000,000, more preferably in the range 30 of 2,000 to 500,000, even more preferably in the range of 3,000 to 100,000.

Further, in a case where the resin (a) has a melting point,

the melting point of the resin (a) is preferably in the range of 20 to 200°C, more preferably in the range of 30 to 90°C, even more preferably in the range of 40 to 80°C.

[0068]

5 Furthermore, the Tg of the resin (a) is preferably in the range of 20 to 200°C, more preferably in the range of 30 to 90°C, even more preferably in the range of 40 to 80°C.

Moreover, the SP value of the resin (a) is preferably in the range of 8 to 16, more preferably in the range of 8.5 to 10 16, even more preferably in the range of 9 to 14.

[0069]

15 The resin particle (A) may contain an additive (T) (e.g., various additives such as a filler, a colorant, a plasticizer, a releasing agent, a charge control agent, a UV absorbing agent, an antioxidant, an anti-static agent, a fire retardant, an antibacterial agent, and a preservative) in addition to the resin (a).

20 The amount of the additive (T) contained in the resin particle (A) can be appropriately set according to the purpose of use thereof, but is preferably in the range of 0.01 to 200wt%, more preferably in the range of 0.2 to 150wt%, even more preferably in the range of 0.1 to 100wt% with respect to the weight of the resin particle (A).

25 Examples of a filler to be added include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, silica sand, clay, talc, wollastonite, diatomite, chromium oxide, ceric oxide, chromic oxide, ceric oxide, colcothar, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium 30 carbonate, calcium carbonate, silicon carbide, and silicon nitride.

[0070]

Examples of a colorant to be added include all the well-known dyes and pigments such as Carbon black, Nigrosine dyes, Iron black, Naphthol yellow S, Hansa yellow (10G, 5G and G), Cadmium yellow, Yellow colored iron oxide, Yellow ochre, 5 Chrome yellow, Titanium yellow, Polyazo yellow, Oily yellow, Hansa yellow (GR, A, RN and R), Pigment yellow L, Benzidine yellow (G and GR), Permanent yellow (NCG), Vulcan fast yellow (5G and R), Tartrazine lake, Quinoline yellow lake, Anthracene yellow BGL, Isoindolinone yellow, Colcothar, Red lead, Orange lead, 10 Cadmium red, Cadmium mercury red, Antimony orange, Permanent red 4R, Para red, Fire red, Parachloroorthonitro aniline red, Lithol fast scarlet G, Brilliant fast scarlet, Brilliant carmine BS, Permanent red (F2R, F4R, FRL, FRLL and F4RH), Fast scarlet VD, Vulcan fast rubine B, Brilliant scarlet G, Lithol rubine 15 GX, Permanent red F5R, Brilliant carmine 6B, Pigment scarlet 3B, Bordeaux 5B, Toluidine maroon, Permanent bordeaux F2K, Helio bordeaux BL, Bordeaux 10B, BON maroon light, BON maroon medium, Eosine lake, Rhodamine lake B, Rhodamine lake Y, Alizarin lake, Thioindigo red B, Thioindigo maroon, Oil red, Quinacridone red, 20 Pyrazolone red, Polyazo red, Chrome vermilion, Benzidine orange, Perynone orange, Oil orange, Cobalt blue, Cerulean blue, Alkali blue lake, Peacock blue lake, Victoria blue lake, metal-free Phthalocyanine blue, Phthalocyanine blue, Fast sky blue, Indanthrene blue (RS, BC), Indigo, Ultramarine, Prussian blue, 25 Anthraquinone blue, Fast violet B, Methyl violet lake, Cobalt violet, Manganese violet, Dioxane violet, Anthraquinone violet, Chrome green, Zinc green, Chromium oxide, Viridian, Emerald green, Pigment green B, Naphthol green B, Green gold, Acid green lake, Malachite green lake, Phthalocyanine green, Anthraquinone green, 30 Titanium oxide, Hydrozincite, Lithopone, and mixtures of two or more of them.

[0071]

Examples of a plasticizer (L) to be added include, but not limited to, the following (L1) to (L5) and mixtures of two or more of them:

5 (L1) phthalic acid esters having 8 to 60 carbon atoms (e.g., dibutyl phthalate, dioctyl phthalate, butyl benzyl phthalate, and diisodecyl phthalate);

(L2) aliphatic dibasic acid esters having 6 to 60 carbon atoms (e.g., di-2-ethylhexyl adipate and 2-ethylhexyl sebacate);

10 [0072]

(L3) trimellitic acid esters having 10 to 70 carbon atoms (e.g., tri-2-ethylhexyl trimellitate and trioctyl trimellitate);

15 (L4) phosphoric acid esters having 6 to 60 carbon atoms (e.g., triethyl phosphate, tri-2-ethylhexyl phosphate, and tricresyl phosphate); and

(L5) fatty acid esters having 8 to 50 carbon atoms (e.g., butyl oleate).

20 Among these plasticizers, (L1), (L2), (L3), and (L4) are preferably used, more preferably (L1), (L2), and (L4), even more preferably (L1) and (L4).

[0073]

25 As a releasing agent, waxes and silicone oils having a kinematic viscosity of 30 to 100,000 cSt at 25°C, and the like can be used.

Examples of a wax to be added include well-known waxes such as polyolefin waxes (e.g., polyethylene wax and polypropylene wax), long-chain hydrocarbon waxes (e.g., paraffin wax and Sasol wax), and carbonyl group-containing waxes.

30 Among these waxes, carbonyl group-containing waxes are preferably used. Examples of the carbonyl group-containing wax include polyalkanoic acid esters (e.g., carnauba wax, montan

wax, trimethylolpropane tribehenate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerin tribehenate, and 1,18-octadecanediol distearate), polyalkanol esters (e.g., tristearyl trimellitate and distearyl maleate),
5 polyalkanoic acid amides (e.g., ethylenediamine dibehenyl amide), polyalkylamides (e.g., tristearylamide trimellitate), and dialkyl ketones (e.g., distearyl ketone). Among these carbonyl group-containing waxes, polyalkanoic acid esters are preferably used.

10 [0074]

Examples of a charge control agent to be added include all the well-known charge control agents such as nigrosine-based dyes, triphenylmethane-based dyes, chromium-containing metal complex dyes, molybdic acid chelate pigments, rhodamine-based dyes, alkoxy-based amines, quaternary ammonium salts (including fluorine-modified quaternary ammonium salts), alkylamides, phosphorus or phosphorus compounds, tungsten or tungsten compounds, fluorine-based activators, metal salts of salicylic acid, and metal salts of salicylic acid derivatives. Specific examples of the charge control agents include Bontron 03 as a nigrosine-based dye, Bontron P-51 as a quaternary ammonium salt, Bontron S-34 as a metal-containing azo dye, E-82 as an oxynaphthoic acid-based metal complex, E-84 as a salicylic acid-based metal complex, E-89 as a phenol-based condensation product, which are manufactured by Orient Chemical Industries, Ltd.; TP-302 and TP-415 as quaternary ammonium salt molybdenum complexes, which are manufactured by Hodogaya Chemical Co., Ltd.; Copy Charge PSY VP2038 as a quaternary ammonium salt, Copy blue PR as a triphenylmethane derivative, Copy Charge NEG VP2036 and 30 Copy Charge NX VP434 as quaternary ammonium salts, which are manufactured by Hoechst; LRA-901 and LR-147 as a boron complex, which are manufactured by Japan Carlit Co., Ltd.; copper

phthalocyanine, perylene, quinacridone, azo-based pigments, and other polymeric compounds having a functional group such as a sulfo group, a carboxyl group, or a quaternary ammonium salt group.

5 [0075]

A method for adding the additive (T) to the resin particles (A) is not limited to any specific one. For example, in the preparing method of resin particles according to the present invention (which will be described later), the additive (T) may 10 be added to an aqueous medium, or a mixture of the resin (a) and the additive (T) may be dispersed in an aqueous medium.

[0076]

In a case where a colorant is added to the resin particles (A) as an additive, the colorant may be one treated with a coupling 15 agent such as a silane coupling agent, a titanium coupling agent, an aluminum coupling agent, or the like.

Particularly, in a case where carbon black is used as a colorant, carbon black treated with an aluminum coupling agent is preferably used.

20 [0077]

As a method for allowing the resin particles (A) to contain a colorant treated with a coupling agent, a method in which a dispersion liquid containing a colorant treated with an aluminum coupling agent is formed to mix it with the resin (a) can be 25 mentioned, for example.

In the formation of a dispersion liquid containing a colorant, it is preferred that the colorant and an aluminum coupling agent are first mixed by a wet method. Mixing of a colorant and an aluminum coupling agent is carried out using 30 an ordinary mixer or agitator. Specifically, a colorant and an aluminum coupling agent are placed in an appropriate container equipped with particulate media such as an Atliter, a ball mill,

a sand mill, a vibration mill, or the like, and then they are agitated. Preferred examples of particulate media to be used include steel such as stainless steel and carbon steel, alumina, zirconia, and silica, and the like. In the process, a temperature 5 within the container is kept at 20 to 160°C, preferably at 20 to 100°C, more preferably at 30 to 60°C. By using such an agitator, it is possible to release the colorant from agglomeration and to disperse the colorant so that the average particle size of the colorant becomes about 0.7 µm or less, preferably about 0.4 10 µm or less and, further, to apply load so that the aluminum coupling agent is made to react with and adsorbed to the colorant. Next, it is preferred that the colorant dispersion liquid is again dispersed by high speed shearing or the like in order to prevent agglomeration of the colorant in the mixing of the colorant 15 dispersion liquid with the binder resin. Dispersion can be carried out by a dispersing machine having a high-speed blade rotation type or forced gap-passing type high-speed shearing system, such as various homomixers, homogenizers, colloidmills, Ultra-Turrax, Clear Mill, or the like.

20 [0078]

The aluminum coupling agent to be used is not limited to any specific one as long as it is a compound capable of coupling with a colorant. Examples of such an aluminum coupling agent include alkyl (having 1 to 30 carbon atoms) acetoacetate aluminum 25 isopropylate, aluminum tris (ethyl acetoacetate), and aluminum monoisopropoxy monooleoxy ethylacetoacetate.

The amount of the aluminum coupling agent to be used is preferably in the range of 0.1 to 100 wt parts with respect to 100 wt parts of the colorant from the viewpoint of dispersibility 30 of the colorant in the resin (a), more preferably 0.1 to 50 wt parts, even more preferably 0.3 to 30 wt parts. That is, the upper limit is preferably 100 wt parts, more preferably 50 wt

parts, even more preferably 30 wt parts. The lower limit is preferably 0.1 wt part, more preferably 0.1 wt part, even more preferably 0.3 wt part.

[0079]

5 A method for preparing an aqueous dispersion (I) containing the resin particles (A) is not limited to any specific one, but examples of such a method include a method in which a precursor of the resin (a) is allowed to react in an aqueous medium, a method in which a dead polymer of the resin (a) is formed to disperse it in an aqueous medium, and a method in which a dead polymer of the resin (a) is dispersed in an aqueous medium, and a precursor of the resin (a) is allowed to react in the aqueous medium.

[0080]

15 Examples of a method, in which a precursor of the resin (a) is allowed to react in an aqueous medium, include the following methods (1) and (2):

20 (1) in a case where vinyl resins are concerned, a method in which an aqueous dispersion of the resin particles (A) is prepared using a monomer as an initial material under the presence of polymerization catalyst by polymerization reaction such as suspension polymerization, emulsion polymerization, seed polymerization, or dispersion polymerization;

[0081]

25 (2) in a case where polyaddition or condensation resins such as polyesters, polyurethanes, and epoxy resins are concerned, a method in which a precursor (a0) of the resin (a) or a solvent solution of the precursor (a0) is dispersed in an aqueous medium under the presence of a suitable dispersant, and is then cured 30 by heating or adding a curing agent (which is a compound having at least 2 functional groups capable of reacting with the precursor in the molecule) to produce an aqueous dispersion of

the resin particles (A).

[0082]

Examples of a method, in which a dead polymer of the resin (a) is formed to disperse it in an aqueous medium, include the 5 following methods (3) to (7):

(3) a method in which the resin (a) produced in advance by polymerization reaction (which may be carried out by any polymerization reaction method such as addition polymerization, ring-opening polymerization, polyaddition, addition 10 condensation, condensation polymerization, or the like) is ground using a mechanical rotary or jet type pulverizer, and is then classified to obtain resin particles (A), and the resin particles (A) are dispersed in water under the presence of a suitable dispersant;

15 [0083]

(4) a method in which a solution of the resin (a) which is produced in advance by polymerization reaction (which may be carried out by any polymerization reaction method such as addition polymerization, ring-opening polymerization, 20 polyaddition, addition condensation, condensation polymerization, or the like) is sprayed in a mist form to obtain resin particles (A) from which the solvent is removed, and the resin particles (A) are dispersed in water under the presence of a suitable dispersant;

25 [0084]

(5) a method in which the resin (a) is in advance produced by polymerization reaction (which may be carried out by any polymerization reaction method such as addition polymerization, ring-opening polymerization, polyaddition, addition 30 condensation, condensation polymerization, or the like), resin particles are precipitated by adding a poor solvent (which is a solvent incapable of dissolving the resin (a) in 1% or more

at 25°C) to a solution of the resin (a) or by cooling a solution of the resin (a) produced in advance by dissolving the resin (a) in a solvent by heating, the solvent is removed to obtain resin particles (A), and the resin particles (A) are dispersed

5 in water under the presence of a suitable dispersant;

[0085]

(6) a method in which a solution of the resin (a) which is produced in advance by polymerization reaction (which may be carried out by any polymerization reaction method such as

10 addition polymerization, ring-opening polymerization, polyaddition, addition condensation, condensation polymerization, or the like) is dispersed in an aqueous medium under the presence of a suitable dispersant, and then the solvent is removed by heating or decompression; and

15 [0086]

(7) a method in which in a solution of the resin (a) which is produced in advance by polymerization reaction (which may be carried out by any polymerization reaction method such as addition polymerization, ring-opening polymerization,

20 polyaddition, addition condensation, condensation polymerization, or the like), a suitable emulsifier is dissolved, then water is added for phase inversion emulsification, and thereafter the solvent is removed by heating or decompression.

25 [0087]

Among the above-described methods (1) to (7), the methods (1), (2), (6), and (7) and a combination of two or more of them are preferable, the methods (1), (2), and (6) and a combination of two or more of them are more preferable, and the methods (2)

30 and (6) and a combination of them are even more preferable.

[0088]

The method in which a precursor of the resin (a) is allowed

to react in an aqueous medium will be described in more detail.

The precursor (a0) of the resin (a) is not limited to any specific one as long as it can be converted to the resin (a) by chemical reaction. For example, in a case where the resin 5 (a) is a vinyl resin, examples of the precursor (a0) include the vinyl monomers mentioned above (which may be used singly or in combination of two or more of them) and solutions thereof.

[0089]

In a case where the vinyl monomer is used as the precursor 10 (a0), examples of the method for allowing the precursor (a0) to react to convert it to the resin (a) include a method in which an oil phase comprised of an oil-soluble initiator, the monomer and, as necessary, a solvent (U) (which will be described later) is dispersed and suspended in water under the presence of a 15 synthetic polymeric dispersant (H) to carry out radical polymerization reaction by heating (that is, the so-called suspension polymerization method), and a method in which an oil phase comprised of the monomer and, as necessary, a solvent (U) is emulsified in water containing an emulsifier and a 20 water-soluble initiator to carry out radical polymerization reaction by heating (that is, the so-called emulsion polymerization method).

[0090]

As the oil-soluble initiator and the water-soluble 25 initiator, peroxide polymerization initiators, and azo polymerization initiators, and the like can be used. A peroxide polymerization initiator may be used in combination with a reducing agent to form a redox polymerization initiator. Further, these initiators can be used in combination of two or 30 more of them.

[0091]

Examples of the peroxide polymerization initiators

include oil-soluble peroxide polymerization initiators and water-soluble peroxide polymerization initiators. As oil-soluble peroxide polymerization initiators, acetyl cyclohexylsulfonyl peroxide, isobutyl peroxide, 5 diisopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, 2,4-dichlorobenzoyl peroxide, t-butyl peroxy pivalate, 3,5,5-trimethylhexanonyl peroxide, octanoyl peroxide, decanoyl peroxide, lauroyl peroxide, stearoyl peroxide, propionitrile peroxide, succinic acid peroxide, 10 acetyl peroxide, t-butyl peroxy-2-ethylhexanoate, benzoyl peroxide, p-chlorobenzoyl peroxide, t-butyl peroxyisobutyrate, t-butyl peroxy maleic acid, t-butyl peroxy laurate, cyclohexanone peroxide, t-butyl peroxyisopropylcarbonate, 15 2,5-dimethyl-2,5-dibenzoylperoxyhexane, t-butyl peroxyacetate, t-butyl peroxybenzoate, diisobutyl diperoxyphthalate, methyl ethyl ketone peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di-t-butylperoxyhexane, t-butylcumyl peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, diisopropylbenzene hydroperoxide, p-menthane 20 hydroperoxide, pinane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, cumene peroxide, and the like can be used.

[0092]

As water-soluble peroxide polymerization initiators, 25 hydrogen peroxide, peracetic acid, ammonium persulfate, potassium persulfate, sodium persulfate, and the like can be used.

[0093]

Examples of the azo polymerization initiators include 30 oil-soluble azo polymerization initiators and water-soluble azo polymerization initiators. As oil-soluble azo polymerization initiators, 2,2'-azobisisobutyronitrile,

1,1'-azobiscyclohexane-1-carbonytrile,
2,2'-azobis-4-methoxy-2,4-dimethylvaleronitrile,
2,2'-azobis-2,4-dimethylvaleronitrile,
dimethyl-2,2'-azobis(2-methylpropionate),
5 1,1'-azobis(1-acetoxy-1-phenylethane),
2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), and the
like can be used.

[0094]

As water-soluble azo polymerization initiators,
10 azobisamidinopropane salt, azobiscyanovaleric acid (salt),
2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], and
the like can be used.

[0095]

As redox polymerization initiators, oil-soluble redox
15 polymerization initiators and water-soluble redox
polymerization initiators can be mentioned.

Examples of the oil-soluble redox polymerization
initiators include combinations of oil-soluble peroxides such
as hydroperoxides (e.g., tert-butyl hydroperoxide and cumene
20 hydroperoxide), dialkyl peroxides (e.g., lauroyl peroxide),
diacyl peroxides (e.g., benzoyl peroxide), and the like and
oil-soluble reducing agents such as tertiary amines (e.g.,
triethylamine and tributylamine), naphthenic acid salts,
mercaptans (e.g., mercaptoethanol and lauryl mercaptan),
25 organic metal compounds (e.g., triethylaluminum, triethylboron,
and diethylzinc), and the like.

[0096]

Examples of the water-soluble redox polymerization
initiators include combinations of water-soluble peroxides such
30 as persulfate salts (e.g., potassium persulfate and ammonium
persulfate), hydrogen peroxide, hydroperoxides (e.g.,
tert-butyl hydroperoxide and cumene hydroperoxide), and the

like and water-soluble inorganic or organic reducing agents such as iron (II) salts, sodium bisulfite, alcohols, and dimethylaniline).

[0097]

5 In a case where the resin (a) is a condensed resin (e.g., polyurethane, an epoxy resin, or polyester), a combination of a reactive group-containing prepolymer (α) (which will be described later) and a curing agent (β) may also be used as the precursor (a0). Here, the word "reactive group" means a group
10 capable of reacting with the curing agent (β).

[0098]

In this case, examples of a method of allowing the precursor (a0) to react to form the resin particles (A) include the following methods (1) to (3):

15 (1) a method in which an oil phase containing the reactive group-containing prepolymer (α), the curing agent (β) and, as necessary, the solvent (U) is dispersed in an aqueous medium, and then the reactive group-containing prepolymer (α) and the curing agent (β) are allowed to react by heating to form the
20 resin particles (A) comprising the resin (a);

[0099]

25 (2) a method in which the reactive group-containing prepolymer (α) or a solution thereof is dispersed in an aqueous medium, and a water-soluble curing agent (β) is added thereto to allow them to react so as to form the resin particles (A) comprising the resin (a); and

30 (3) a method in which the reactive group-containing prepolymer (α) or a solution thereof is dispersed in an aqueous medium to allow the reactive group-containing prepolymer (α) to react with water to form the resin particles (A) comprising the resin (a), the method being applicable to a case where the reactive group-containing prepolymer (α) can be cured by the

reaction with water.

[0100]

Examples of a combination of the reactive group contained in the reactive group-containing prepolymer (α) and the curing agent (β) include the following combinations (1) and (2):

5 combination (1) a combination of a reactive group-containing prepolymer (α_1) having a functional group capable of reacting with an active hydrogen-containing group and an active hydrogen-containing compound (β_1) which may be
10 blocked with a removal compound; and

15 combination (2) a combination of a reactive group-containing prepolymer (α_2) having an active hydrogen-containing group, and a curing agent (β_2) having a functional group capable of reacting with an active hydrogen-containing group.

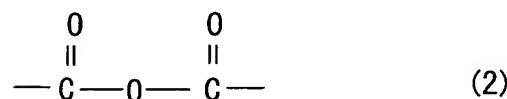
Among these combinations, the combination (1) is preferably used from the viewpoint of reaction rate in water.

[0101]

Examples of a functional group capable of reacting with an active hydrogen-containing group include an isocyanate group, a blocked isosyanate group, an epoxy group, an acid anhydride group (a group expressed by the general formula (2)), and an acid halide group (a group expressed by the general formula (3)).

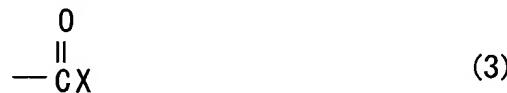
[0102]

25 [Chem. 2]



[0103]

[Chem. 3]



Wherein X represents halogen (such atoms as, for example, F, Cl, Br and Br).

[0104]

Among them, an isocyanate group, a blocked isocyanate group, 5 and an epoxy group are preferably used, more preferably an isocyanate group and a blocked isocyanate group.

In this regard, it is to be noted that the blocked isocyanate group means an isocyanate group that is blocked with a blocking agent.

10 [0105]

Examples of the blocking agent include well-known blocking agents such as oximes (e.g., acetoxime, methyl isobutyl ketoxime, diethyl ketoxime, cyclopentanone oxime, cyclohexanone oxime and methyl ethyl ketoxime), lactams (e.g., γ -butyrolactam, 15 ϵ -caprolactam, and γ -valerolactam), aliphatic alcohols having 1 to 20 carbon atoms (e.g., ethanol, methanol, and octanol), phenols (e.g., phenol, m-cresol, xylenol, and nonylphenol), active methylene compounds (e.g., acetylacetone, ethyl malonate, and ethyl acetoacetate), basic nitrogen-containing compounds 20 (e.g., N,N-diethylhydroxylamine, 2-hydroxypyridine, pyridine N-oxide, and 2-mercaptopypyridine), and mixtures of two or more of them.

Among these blocking agents, oximes are preferably used, more preferably methyl ethyl ketoxime.

25 [0106]

As the skeleton of the reactive group-containing prepolymer (α), polyethers, polyesters, epoxy resins, or polyurethanes can be used.

Among them, polyesters, epoxy resins, and polyurethanes 30 are preferably used, more preferably polyesters and polyurethanes.

[0107]

Examples of polyethers include polyethylene oxide, polypropylene oxide, polybutylene oxide, and polytetramethylene oxide.

5 Examples of polyesters include polycondensation products of the diols (11) and the dicarboxylic acids (13), and polylactones (e.g., the ring-opening polymerization product of ϵ -caprolactone).

10 Examples of epoxy resins include addition-condensation products of bisphenols (e.g., bisphenol A, bisphenol F, and bisphenol S) and epichlorohydrine.

Examples of polyurethanes include polyaddition products of the diols (11) and the polyisocyanates (15), and polysddition products of the polyesters and the polyisocyanates (15).

[0108]

15 A method of introducing the above mentioned reactive group into the polyester, the epoxy resin, or the polyurethane is not limited to any specific one, but examples of such a method include the following methods (1) and (2):

20 (1) a method in which one of components constituting the polyester, the epoxy resin, or the polyurethane is used excessively to allow a reactive group of the component to remain; and

25 (2) a method in which one of components constituting the polyester, the epoxy resin, or the polyurethane is used excessively to allow a functional group of the component to remain, and then the functional group is further reacted with a compound having a functional group (reactive group) capable of reacting with the remaining functional group.

[0109]

30 According to the method (1), it is possible to obtain a hydroxyl group-containing polyester prepolymer, a carboxyl group-containing polyester prepolymer, an acid halide

group-containing polyester prepolymer, a hydroxyl group-containing epoxy resin prepolymer, an epoxy group-containing epoxy resin prepolymer, a hydroxyl group-containing polyurethane prepolymer, and an isocyanate group-containing polyurethane prepolymer, and the like.

5 [0110]

For example, in the case of a hydroxyl group-containing polyester prepolymer, the ratio between the components in the method (1), that is, the ratio between the alcohol components (e.g., the diols (11) and the polyols (12)) and the carboxylic acid components (e.g., the dicarboxylic acids (13) and the polycarboxylic acids (14)) as expressed in terms of the equivalent ratio of hydroxyl group [OH] to carboxyl group [COOH], that is, the equivalent ratio [OH]/[COOH] is preferably in the 10 range of 2/1 to 1/1, more preferably in the range of 1.5/1 to 1/1, even more preferably in the range of 1.3/1 to 1.02/1. That is, the upper limit of the mole ratio [OH]/[COOH] is preferably 15 2/1, more preferably 1.3/1, the lower limit is preferably 1/1, more preferably 1.02/1.

20 In each of the cases of a carboxyl group-containing polyester prepolymer, an acid halide group-containing polyester prepolymer, a hydroxyl group-containing polyurethane prepolymer, and an isocyanate group-containing polyurethane prepolymer, components thereof are different from those of the 25 example case, but a preferred ratio between the components is the same as described above.

[0111]

According to the method (2), an isocyanate group-containing prepolymer can be obtained by allowing a 30 prepolymer obtained by the method (1) to react with polyisocyanate, a blocked isocyanate group-containing prepolymer can be obtained by allowing a prepolymer obtained

by the method (1) to react with blocked polyisocyanate, an epoxy group-containing prepolymer can be obtained by allowing a prepolymer obtained by the method (1) to react with polyepoxide, and an acid anhydride group-containing prepolymer can be obtained
5 by allowing a prepolymer obtained by the method (1) to react with a compound having 2 or more acid anhydride groups.

[0112]

For example, in the case of obtaining an isocyanate group-containing polyester prepolymer by allowing a hydroxyl group-containing polyester to react with polyisocyanate according to the method (2), the amount of the compound having a reactive group to be used, that is, the ratio between the hydroxyl group-containing polyester and polyisocyanate to be used as expressed in terms of the equivalent ratio of isocyanate group
15 $[NCO] / \text{hydroxyl group } [OH]$, that is, the equivalent ratio $[NCO]/[OH]$ is preferably in the range of 5/1 to 1/1, more preferably in the range of 4/1 to 1.2/1, even more preferably in the range of 2.5/1 to 1.5/1. That is, the upper limit of the mole ratio $[NCO]/[OH]$ is preferably 5/1, more preferably
20 4/1, even more preferably 2.5/1, the lower limit is preferably 1/1, more preferably 1.2/1, even more preferably 1.5/1.

In each of the cases of other prepolymers, components thereof are different from those of the example case, but a preferred ratio between the components is the same as described
25 above.

[0113]

The average number of the reactive group per molecule contained in the reactive group-containing prepolymer (α) is preferably in the range of 1 to 3, more preferably in the range
30 of 1.5 to 3, even more preferably in the range of 1.8 to 2.5. By setting the average number of the reactive group per molecule contained in the reactive group-containing prepolymer (α) to

a value within the above range, it is possible for the resin (a) obtained by the reaction with the curing agent (β) to have high mechanical strength.

[0114]

5 The Mn of the reactive group-containing prepolymer (a) is preferably in the range of 500 to 30,000, more preferably 1,000 to 20,000, even more preferably 2,000 to 10,000. That is, the upper limit is preferably 30,000, more preferably 20,000, even more 10,000, the lower limit is preferably 500, more 10 preferably 1,000, even more 2,000.

The Mw of the reactive group-containing prepolymer (a) is preferably in the range of 1,000 to 50,000, more preferably 2,000 to 40,000, even more preferably 4,000 to 20,000. That is, the upper limit of Mw is preferably 50,000, more preferably 15 40,000, even more preferably 20,000, the lower limit is preferably 1,000, more preferably 2,000, even more preferably 4,000.

[0115]

As the active hydrogen group-containing compounds (β 1), 20 polyamines which may be blocked with removable compounds and polyols which may be blocked with removable compounds can be mentioned, in addition to the above mentioned water, the diols (11), the polyols (12) having 3 to 6 or more hydroxyl groups, the dicarboxylic acids (13), the polycarboxylic acids (14) having 25 3 to 4 or more carboxyl groups, the polyamines (16), and the polythiols (17).

[0116]

Examples of a polyamine blocked with a removable compound include ketimine compounds obtained by dehydration between the 30 polyamines (16) and ketones having 3 to 8 carbon atoms (e.g., acetone, methyl ethyl ketone, and methyl isobutyl ketone), aldimine compounds obtained by dehydration between the

polyamines (16) and aldehyde compounds having 2 to 8 carbon atoms (e.g., formaldehyde and acetaldehyde), enamine compounds obtainable from the polyamines (16) and ketones having 3 to 8 carbon atoms or aldehydes having 2 to 8 carbon atoms, and

5 oxazolidine compounds.

[0117]

Among these, polyamines which may be blocked, polyols which may be blocked, and water are preferably used, more preferably polyamines which may be blocked and water, even more preferably

10 polyamines, ketimine compounds and water, most preferably 4,4'-diaminodiphenylmethane, xylylenediamine, isophoronediamine, ethylenediamine, diethylenetriamine, triethylenetetramine, ketimine compounds obtainable from these polyamines and ketones, and water.

15 [0118]

When the resin particles (A) are produced, a reaction terminator (β s) may be used as necessary together with the active hydrogen group-containing compound (β 1). By using the reaction terminator (β s) and the active hydrogen group-containing

20 compound (β 1) together in a certain ratio, it becomes easy to control the molecular weight of the resin (a) comprising the resin particles (A).

[0119]

Examples of such a reaction terminator (β s) include

25 monoamines having 1 to 40 carbon atoms (e.g., diethylamine, dibutylamine, butylamine, laurylamine, monoethanolamine, and diethanolamine), blocked monoamines having 3 to 40 carbon atoms (e.g., ketimine compounds), monoools having 1 to 40 carbon atoms (e.g., methanol, ethanol, isopropanol, butanol, and phenol),

30 monomercaptans having 2 to 40 carbon atoms (e.g., butylmercaptan and laurylmercaptan), monoisocyanates having 5 to 40 carbon atoms (e.g., butyl isocyanate, lauryl isocyanate, and phenyl

isocyanate), and monoepoxides having 2 to 40 carbon atoms (e.g., butyl glycidyl ether).

[0120]

In the combination (2) described above (that is, in the 5 combination of the reactive group-containing prepolymer (α_2) having an active hydrogen-containing group and the curing agent (β_2) having a functional group capable of reacting with an active hydrogen-containing group), examples of the active hydrogen-containing group contained in the reactive 10 group-containing prepolymer (α) include an amino group, hydroxyl groups (an alcoholic hydroxyl group and a phenolic hydroxyl group), a mercapto group, a carboxyl group, and organic groups obtained by blocking these groups with removable compounds (e.g., ketones and aldehydes) (e.g., a ketimine-containing group, an 15 aldimine-containing group, an oxazolidine-containing group, an enamine-containing group, an acetal-containing group, a ketal-containing group, a thioacetal-containing group, and a thioketal-containing group).

Among these active hydrogen-containing groups, an amino 20 group, hydroxyl groups, and organic groups obtained by blocking these groups with removable compounds are preferably used, more preferably hydroxyl groups.

[0121]

Examples of the curing agent (β_2) having a functional group 25 capable of reacting with an active hydrogen-containing group include the polyisocyanates (15), the polyepoxides (18), the dicarboxylic acids (13), the polycarboxylic acids (14), compounds having two or more acid anhydride groups, and compounds having two or more acid halide groups.

30 Among these, the polyisocyanates and the polyepoxides are preferably used, more preferably the polyisocyanates.

[0122]

Examples of the compound having two or more acid anhydride groups include a (co)polymer of pyromellitic anhydride and polymaleic anhydride, and the like.

5 Examples of the compound having two or more acid halide groups include acid halides (e.g., acid chloride, acid bromide, and acid iodide) of the dicarboxylic acids (13) or the polycarboxylic acids (14).

When the resin particles (A) are produced, the reaction 10 terminator (β_1) may be used as necessary together with the curing agent (β_2) having a functional group capable of reacting with an active hydrogen-containing group. By using the reaction terminator (β_1) and the curing agent (β_2) together in a certain ratio, it becomes easy to control the molecular weight of the resin (a) constituting the resin particles (A).

15 [0123]

The amount of the curing agent (β) to be used as expressed in terms of the ratio $[\alpha]/[\beta]$ of the equivalent of the reactive group $[\alpha]$ in the reactive group-containing prepolymer (α) to the equivalent of the active hydrogen-containing group $[\beta]$ in 20 the curing agent (β) is preferably in the range of 1/2 to 2/1, more preferably in the range of 1.5/1 to 1/1.5, even more preferably in the range of 1.2/1 to 1/1.2. That is, the upper limit of the ratio $[\alpha]/[\beta]$ is preferably 2/1, more preferably 1.5/1, even more preferably 1.2/1, the lower limit is preferably 25 1/2, more preferably 1/1.5, even more preferably 1/1.2.

In a case where water is used as the curing agent (β), water is considered as a bifunctional active hydrogen-containing compound.

[0124]

30 The length of time of reaction between the reactive group-containing prepolymer (α) and the curing agent (β) is selected according to reactivity that depends on the combination

of the kind of reactive group contained in the prepolymer (α) and the curing agent (β), but is preferably in the range of 10 minutes to 40 hours, more preferably in the range of 30 minutes to 24 hours, even more preferably in the range of 30 minutes 5 to 8 hours.

Further, the temperature of the reaction is preferably in the range of 0 to 150°C, more preferably in the range of 50 to 120°C.

As necessary, a well-known catalyst can be used.

10 Specifically, in the case of the reaction between isocyanate and an active hydrogen-containing compound by way of example, dibutyltin laurate, dioctyltin laurate or the like can be used.
[0125]

15 As the emulsifier and the dispersant used in the above-mentioned methods (1) to (7) for obtaining the aqueous dispersant (I), well-known surfactants (S) and synthetic polymeric dispersants (H), and the like can be mentioned.

20 In a case where the surfactant (S) is used, the amount thereof to be used is preferably in the range of 0.0001 to 50wt%, more preferably in the range of 0.0005 to 0.4wt%, even more preferably in the range of 0.001 to 0.3wt% with respect to the weight of the resin (a) and the precursor thereof (a0).
[0126]

25 In a case where the synthetic polymeric dispersant (H) is used, the amount thereof to be used is preferably in the range of 0.005 to 0.6wt%, more preferably in the range of 0.01 to 0.4wt%, even more preferably in the range of 0.02 to 0.3wt% with respect to the weight of the resin (a) and the precursor thereof (a0).
[0127]

30 Further, the plasticizer (L) or the like may be used as an emulsifier assistant or a dispersant assistant.

In a case where the plasticizer (L) is used, the amount

thereof to be used is preferably in the range of 0.01 to 0.3wt%, more preferably in the range of 0.02 to 0.25wt%, even more preferably in the range of 0.03 to 0.2wt% with respect to the weight of the resin (a) and the precursor thereof (a0).

5 The plasticizer (L) may be added as necessary to either water or the resin (a) at dispersion-emulsification.

[0128]

10 As surfactants (S), anionic surfactants (S-1), cationic surfactants (S-2), amphoteric surfactants (S-3), and nonionic surfactants (S-4), and the like can be used. In this regard, it is to be noted that these surfactants (S) can be used in combination of two or more of them.

[0129]

15 Examples of the anionic surfactant (S-1) include carboxylic acids or salts thereof, sulfuric acid ester salts, salts of carboxymethylation products, sulfonic acid salts, and phosphoric acid ester salts.

[0130]

20 As carboxylic acids or salts thereof, saturated or unsaturated fatty acids having 8 to 22 carbon atoms or salts thereof can be used, and examples of such carboxylic acids include capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, oleic acid, linoleic acid, ricinoleic acid, and mixtures of higher fatty acids obtained 25 by saponifying coconut oil, palm kernel oil, rice bran oil, beef tallow, and the like.

30 As the salts of these carboxylic acids, sodium salts, potassium salts, amine salts, ammonium salts, quaternary ammonium salts, and alkanolamine salts (e.g., monoethanolamine salt, diethanolamine salt, and triethanolamine salt), and the like can be mentioned.

[0131]

As sulfuric acid ester salts, higher alcohol sulfuric acid ester salts (C₈-C₁₈ aliphatic alcohol sulfuric acid ester salts), higher alkyl ether sulfuric acid ester salts (C₈-C₁₈ aliphatic alcohol-EO or PO (1 to 10 mol) adduct sulfuric acid ester salts),
5 sulfated oils (which are obtained by directly sulfating and neutralizing naturally-occurring unsaturated fats and oils having 12 to 50 carbon atoms or unsaturated waxes), sulfated fatty acid esters (which are obtained by sulfating and neutralizing lower alcohol (having 1 to 8 carbon atoms) esters
10 of unsaturated fatty acids(having 6 to 40 carbon atoms)), and sulfated olefins (which are obtained by sulfating and neutralizing olefins having 12 to 18 carbon atoms), and the like can be used.

As the salts, sodium salts, potassium salts, amine salts,
15 ammonium salts, quaternary ammonium salts, alkanolamine salts (e.g., monoethanolamine salt, diethanolamine salt, and triethanolamine salt), and the like can be mentioned.

[0132]

Examples of the higher alcohol sulfuric acid ester salts
20 include salts of octyl alcohol sulfate, salts of decyl alcohol sulfate, salts of lauryl alcohol sulfate, salts of stearyl alcohol sulfate, sulfuric acid ester salts of alcohols synthesized using a Ziegler catalyst (e.g., "ALFOL 1214" which is a product of CONDEA), and sulfuric acid ester salts of alcohols
25 synthesized by oxo process (e.g., "Dobanol 23, 25, 45" and "Diadol 115-L, 115-H, 135" which are products of Mitsubishi Chemical Corporation, "Tridecanol" which is a product of Kyowa Hakko Kogyo Co., Ltd., and "Oxocol 1213, 1215, 1415" which are products of Nissan Chemical Industries, Ltd.).

30 [0133]

Examples of the higher alkyl ether sulfuric acid ester salts include lauryl alcohol-ethylene oxide (2 mol) adduct

sulfuric acid ester salts, and octyl alcohol-ethylene oxide (3 mol) adduct sulfuric acid ester salts.

Examples of the sulfated oil include salts of sulfation products of castor oil, arachis oil, olive oil, rape oil, beef 5 tallow, mutton tallow, and the like.

Examples of the sulfated fatty acid ester include salts of sulfation products of butyl oleate, butyl ricinoleate, and the like.

An example of the sulfated olefins includes Teepol (which 10 is a product of Shell Co.).

[0134]

As salts of carboxymethylation products, salts of carboxymethylation products of aliphatic alcohols having 8 to 16 carbon atoms, salts of carboxymethylation products of C₈-C₁₆ 15 aliphatic alcohol-ethylene oxide or propylene oxide (1 to 10 mol) adducts, and the like can be used.

[0135]

Examples of the salts of carboxymethylation products of aliphatic alcohols include a sodium salt of carboxymethylated 20 octyl alcohol, a sodium salt of carboxymethylated decyl alcohol, a sodium salt of carboxymethylated lauryl alcohol, a sodium salt of carboxymethylated Dobanol 23, and a sodium salt of carboxymethylated tridecanol.

[0136]

Examples of the salts of carboxymethylation products of aliphatic alcohol-ethylene oxide (1 to 10 mol) adducts include 25 a sodium salt of carboxymethylation product of octyl alcohol-ethylene oxide (3 mol) adduct, a sodium salt of carboxymethylation product of lauryl alcohol-ethylene oxide (4 mol) adduct, a sodium salt of carboxymethylation product of Dobanol 23- ethylene oxide (3 mol) adduct, and a sodium salt 30 of carboxymethylation product of tridecanol- ethylene oxide (5

mol) adduct.

[0137]

As sulfonic acid salts, alkylbenzene sulfonates, alkylnaphthalene sulfonates, sulfosuccinic acid diester salts, 5 α -olefin sulfonates, Igepon T type, other sulfonates of aromatic ring-containing compounds, and the like can be used.

An example of the alkylbenzene sulfonates includes sodium dodecylbenzensulfonate.

[0138]

10 An example of the alkylnaphthalene sulfonates includes sodium dodecylnaphthalenesulfonate.

An example of the sulfosuccinic acid diesters salts includes sodium di-2-ethylhexyl sulfosuccinate.

15 Examples of the sulfonates of aromatic ring-containing compounds include alkylated diphenyl ether mono- or disulfonate and styrenated phenol sulfonate.

[0139]

As phosphoric acid ester salts, higher alcohol phosphoric acid ester salts, higher alcohol- ethylene oxide adduct 20 phosphoric acid ester salts, and the like can be used.

Examples of the higher alcohol phosphoric acid ester salts include lauryl alcohol phosphoric acid monoester disodium salt, and lauryl alcohol phosphoric acid diester sodium salt.

25 An example of the higher alcohol- ethylene oxide adduct phosphoric acid ester salts includes oleyl alcohol- ethylene oxide (5 mol) adduct phosphoric acid monoester disodium salt.

[0140]

30 As cationic surfactants (S-2), quaternary ammonium salt-type surfactants, amine salt-type surfactants, and the like can be used.

The quaternary ammonium salt-type surfactants can be obtained by the reaction between tertiary amines having 3 to

40 carbon atoms and quaternizing agents (e.g., alkylating agents such as methyl chloride, methyl bromide, ethyl chloride, benzyl chloride, and dimethyl sulfate, and ethylene oxide), and examples of such quaternary ammonium salt-type surfactants include

5 lauryltrimethylammonium chloride, didecyldimethylammonium chloride, dioctyldimethylammonium bromide, stearyltrimethylammonium bromide,

10 lauryldimethylbenzylammonium chloride (benzalkonium chloride), cetylpyridinium chloride, polyoxyethylentrimethylammonium chloride, and stearamidoethyldiethylmethylethylammonium methosulfate.

[0141]

The amine salt-type surfactants can be obtained by neutralizing primary to tertiary amines with inorganic acid (e.g., 15 hydrochloric acid, nitric acid, sulfuric acid, hydrogen iodide, phosphoric acid, or perchloric acid) or organic acid (e.g., acetic acid, formic acid, oxalic acid, lactic acid, gluconic acid, adipic acid, alkylphosphoric acid having 2 to 24 carbon atoms, malic acid, or citric acid).

20 Examples of primary amine salt-type surfactants include inorganic or organic acid salts of aliphatic higher amines having 8 to 40 carbon atoms (e.g., higher amines such as laurylamine, stearylamine, cetylamine, hydrogenated beef tallow amine, and rosin amine), and C₈-C₄₀ higher fatty acid (e.g., stearic acid 25 and oleic acid) salts of lower amines having 2 to 6 carbon atoms.

[0142]

Examples of secondary amine salt-type surfactants include inorganic or organic acid salts of aliphatic amine (having 4 to 40 carbon atoms)-ethylene oxide adducts.

30 Examples of tertiary amine salt-type surfactants include inorganic or organic acid salts of aliphatic amines having 4 to 40 carbon atoms (e.g., triethylamine, ethyldimethylamine,

and N,N,N',N'-tetramethylethylenediamine), aliphatic amines (having 2 to 40 carbon atoms)-ethylene oxide (2 or more mol) adducts, alicyclic amines having 6 to 40 carbon atoms (e.g., N-methylpyrrolidine, N-methylpiperidine,

5 N-methylhexamethyleneimine, N-methylmorpholine, and 1,8-diazabicyclo(5,4,0)-7-undecene), nitrogen-containing heterocyclic aromatic amines having 5 to 30 carbon atoms (e.g., 4-dimethylaminopyridine, N-methylimidazole, and 4,4'-dipyridyl), and inorganic or organic acid salts of tertiary 10 amines such as triethanolamine monostearate, stearamidoethyldiethylmethylethanolamine, and the like.

[0143]

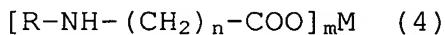
As amphoteric surfactants (S-3), carboxylic acid salt-type amphoteric surfactants, sulfuric acid ester salt-type 15 amphoteric surfactants, sulfonic acid salt-type amphoteric surfactants, phosphoric acid ester salt-type amphoteric surfactants, and the like can be used.

[0144]

As the carboxylic acid salt-type amphoteric surfactants, 20 amino acid-based amphoteric surfactants, betaine-type amphoteric surfactants, and imidazoline-type amphoteric surfactants, and the like can be used. The amino acid-type amphoteric surfactant is an amphoteric surfactant having an amino group and a carboxyl group in the molecule, and examples of such 25 amino acid-type amphoteric surfactant include compounds represented by the general formula (4).

[0145]

[Chem. 4]



30 (wherein R represents a monovalent hydrocarbon group, n is 1 or 2, m is 1 or 2, and M represents a hydrogen ion, an alkali metal ion, an alkaline-earth metal ion, an ammonium cation, an

amine cation, an alkanolamine cation, or the like.)

[0146]

Examples of the amphoteric surfactants represented by the general formula (4) include alkyl (having 6 to 40 carbon atoms) 5 aminopropionic acid-type amphoteric surfactants (e.g., sodium stearylaminopropionate and sodium laurylaminopropionate) and alkyl (having 4 to 24 carbon atoms) aminoacetic acid-type amphoteric surfactants (e.g., sodium laurylamoacetate).

[0147]

10 The betaine-type amphoteric surfactant is an amphoteric surfactant having a quaternary ammonium salt-type cationic moiety and a carboxylic acid-type anionic moiety in the molecule, and examples of such a betaine-type amphoteric surfactant include alkyl (having 6 to 40 carbon atoms) dimethylbetaines (e.g., 15 stearyldimethylaminoacetic acid betaine and lauryldimethylaminoacetic acid betaine), amido betaines having 6 to 40 carbon atoms (e.g., coco-fatty acid amidopropyl betaine), and alkyl (having 6 to 40 carbon atoms) dihydroxyalkyl (having 6 to 40 carbon atoms) betaines (e.g., lauryldihydroxyethyl 20 betaine).

[0148]

25 The imidazoline-type amphoteric surfactant is an amphoteric surfactant having a cationic moiety containing an imidazoline ring and a carboxylic acid-type anionic moiety, and an example of such an imidazoline-type amphoteric surfactant includes

2-undecyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine.

[0149]

30 As other amphoteric surfactants, glycine-type amphoteric surfactants such as sodium lauroyl glycine, sodium lauryl diaminoethylglycine, lauryldiaminoethylglycine hydrochloride,

and dioctyldiaminoethylglycine hydrochloride, sulfobetaine-based amphoteric surfactants such as pentadecylsulfotaurine, sulfonic acid salt-type amphoteric surfactants, and phosphoric acid ester salt-type amphoteric surfactants, and the like can be used.

5 [0150]

As nonionic surfactants (S-4), alkylene oxide adduct-type nonionic surfactants and polyhydric alcohol-type nonionic surfactants, and the like can be used.

10 The alkylene oxide adduct-type nonionic surfactants can be obtained by directly adding alkylene oxide (having 2 to 20 carbon atoms) to higher alcohols having 8 to 40 carbon atoms, higher fatty acids having 8 to 40 carbon atoms or alkylamines having 8 to 40 carbon atoms, or by reacting higher fatty acids 15 with polyalkylene glycols obtained by adding alkylene oxide to glycol, or by adding alkylene oxide to esterification products obtained by the reaction of polyhydric alcohols and higher fatty acids, or by adding alkylene oxide to higher fatty acid amides.

5 [0151]

20 Examples of alkylene oxide include ethylene oxide, propylene oxide, and BO.

Among them, ethylene oxide, and a random or block adduct of ethylene oxide and propylene oxide are preferably used.

25 The number of mols of the alkylene oxide to be added is preferably in the range of 10 to 50 mols, and 50 to 100% of the added alkylene oxide is preferably ethylene oxide.

[0152]

30 Examples of the alkylene oxide adduct-type nonionic surfactants include oxyalkylene(C₂-C₂₄) alkyl(C₈-C₄₀) ethers (e.g., octyl alcohol-ethylene oxide (20 mol) adduct, lauryl alcohol- ethylene oxide (20 mol) adduct, stearyl alcohol- ethylene oxide (10 mol) adduct, oleyl alcohol- ethylene oxide

(5 mol) adduct, and lauryl alcohol- ethylene oxide (10 mol)/propylene oxide (20 mol) block adduct), polyoxyalkylene (C₂-C₂₄) higher fatty acid (C₈-C₄₀) esters (e.g., stearic acid-ethylene oxide (10 mol) adduct and lauric acid-ethylene oxide (10 mol) adduct), higher fatty acid (C₈-C₄₀) esters of polyoxyalkylene (C₂-C₂₄) polyhydric alcohols (C₃-C₄₀), (e.g., polyethylene glycol (Degree of polymerization of 20) lauric acid diester, polyethylene glycol (Degree of polymerization of 20) oleic acid diester, and polyethylene glycol (Degree of polymerization of 20) stearic acid diester), polyoxyalkylene (C₂-C₂₄) alkyl (C₈-C₄₀) phenyl ethers (e.g., nonylphenol-ethylene oxide (4 mol) adduct, nonylphenol-ethylene oxide (8 mol)/propylene oxide (20 mol) block adduct, octylphenol- ethylene oxide (10 mol) adduct, bisphenol A-ethylene oxide (10 mol) adduct, dinonylphenol- ethylene oxide (20 mol) adduct, and styrenated phenol- ethylene oxide (20 mol) adduct), polyoxyalkylene (C₂-C₂₄) alkyl (C₈-C₄₀) amino ethers (e.g., laurylamine- ethylene oxide (10 mol) adduct and stearylamine-ethylene oxide (20 mol) adduct), and polyoxyalkylene (C₂-C₂₄) alkanolamides (in which amide (acyl moiety) has 8 to 24 carbon atoms) (e.g., hydroxyethyl laurylamine- ethylene oxide (10 mol) adduct, hydroxypropyl laurylamine- ethylene oxide (20 mol) adduct, and dihydroxyethyl laurylamine- ethylene oxide (10 mol) adduct).
[0153]

As polyhydric alcohol-type nonionic surfactants, polyhydric alcohol fatty acid esters, polyhydric alcohol fatty acid ester-AO adducts, polyhydric alcohol alkyl ethers, polyhydric alcohol alkyl ether-AO adducts, and the like can be used. Here, polyhydric alcohols have 3 to 24 carbon atoms, fatty acids have 8 to 40 carbon atoms, and AO has 2 to 24 carbon atoms.

[0154]

Examples of the polyhydric alcohol fatty acid esters

include pentaerythritol monolaurate, pentaerythritol monooleate, sorbitan monolaurate, sorbitan monostearate, sorbitan monolaurate, sorbitan dilaurate, sorbitan dioleate, and sucrose monostearate.

5 [0155]

Examples of the polyhydric alcohol fatty acid ester-AO adducts include ethylene glycol monooleate-ethylene oxide (10 mol) adduct, ethylene glycol monostearate- ethylene oxide (20 mol) adduct, trimethylolpropane monostearate- ethylene oxide (20 mol) PO (10 mol) random adduct, sorbitanmonolaurate- ethylene oxide (10 mol) adduct, sorbitan monostearate- ethylene oxide (20 mol) adduct, sorbiatn distearate- ethylene oxide (20 mol) adduct, and sorbitan dilaurate- ethylene oxide (12 mol) PO (24 mol) random adduct.

15 [0156]

Examples of the polyhydric alcohol alkyl ethers include pentaerythritol monobutyl ether, pentaerythritol monolauryl ether, sorbitan monomethyl ether, sorbitan monostearyl ether, methyl glycoside, and lauryl glycoside.

20 [0157]

Examples of the polyhydric alcohol alkyl ether-AO adducts include sorbitan monostearyl ether- ethylene oxide (10 mol) adduct, methyl glycoside- ethylene oxide (20 mol) PO (10 mol) random adduct, lauryl glycoside- ethylene oxide (10 mol) adduct, 25 and stearyl glycoside- ethylene oxide (20 mol) PO (20 mol) random adduct.

[0158]

Examples of the synthetic polymeric dispersants (H) include polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene 30 glycol, polyethylene imine, and water-soluble polyurethanes (e.g., reaction products of polyethylene glycol or polycaprolactone diol with polyisocyanates).

[0159]

Examples of the solvents (U) used in the methods (1) to (7) to obtain the aqueous dispersant (I) include aromatic hydrocarbon solvents (e.g., toluene, xylene, ethylbenzene, and 5 tetralin), aliphatic or alicyclic hydrocarbon solvents (e.g., n-hexane, n-heptane, mineral spirit, and cyclohexane), halogen-containing solvents (e.g., methyl chloride, methyl 10 bromide, methyl iodide, methylene dichloride, carbon tetrachloride, trichloroethylene, and perchloroethylene), ester or ester ether solvents (e.g., ethyl acetate, butyl acetate, methoxybutyl acetate, methylcellosolve acetate, and ethylcellosolve acetate), ether solvents (e.g., diethyl ether, tetrahydrofuran, dioxane, ethylcellosolve, butylcellosolve, and propylene glycol monomethyl ether), ketone solvents (e.g., 15 acetone, methyl ethyl ketone, methyl isobutyl ketone, di-n-butyl ketone, and cyclohexanone), alcohol solvents (e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, 2-ethylhexyl alcohol, and benzyl alcohol), amide solvents (e.g., dimethylformamide and dimethylacetamide), 20 sulfoxide solvents (e.g., dimethylsulfoxide), heterocyclic compound solvents (e.g., N-methylpyrrolidone), and mixtures of two or more of them.

[0160]

Among these solvents, from the viewpoint of easiness of 25 removing solvents, aromatic hydrocarbon solvents, halogen-containing solvents, ester or ester ether solvents, ketone solvents, and alcohol solvents are preferably used, more preferably ester or ester ether solvents, ketone solvents and alcohol solvents.

30 [0161]

The plasticizer (L) to be used is not limited to any specific one, and the above-mentioned plasticizers (L1) to (L5) and

mixtures of two or more of them can be used. A preferred range of the amount of the plasticizer to be used is the same as described above.

[0162]

5 The amount of an aqueous medium to be used with respect to 100 wt parts of the resin (a) is preferably in the range of 50 to 2,000 wt parts, more preferably in the range of 100 to 1,000 wt parts, even more preferably in the range of 100 to 500 wt parts. If the amount of an aqueous medium to be used is less
10 than above lower limit, dispersibility of the resin (a) tends to be lowered. On the other hand, if the amount of an aqueous medium to be used exceeds the above upper limit, economic problems tend to arise.

[0163]

15 It should be noted that the aqueous medium is not limited to any specific one as long as it is a liquid containing water as an essential component. Examples of such an aqueous medium include water, aqueous solutions of solvents, aqueous solutions of the surfactants (S), aqueous solutions of the synthetic
20 polymeric dispersants (H), and mixtures of two or more of them.

25 Examples of the solvents include, among the solvents (U) mentioned above, ester or ester ether solvents, ether solvents, ketone solvents, alcohol solvents, amide solvents, sulfoxide solvents, heterocyclic compound solvents, and mixtures of two or more of them.

30 In a case where the aqueous medium contains such a solvent, the amount of the solvent contained in the aqueous medium is preferably in the range of 5 to 80wt%, more preferably in the range of 2 to 70wt%, even more preferably in the range of 1 to 30wt% with respect to the weight of the aqueous medium. That is, in this case, the upper limit of the amount of the solvent is preferably 80wt%, more preferably 70wt%, even more preferably

30wt%, the lower limit is preferably 5 wt%, more preferably 2 wt%, even more preferably 1 wt%.

[0164]

In a case where the surfactant (S) is used, the amount of the surfactant (S) contained in the aqueous medium is preferably in the range of 0.001 to 0.3wt%, more preferably in the range of 0.005 to 0.2wt%, even more preferably in the range of 0.01 to 0.15wt% with respect to the weight of the aqueous medium.

10 [0165]

In a case where the synthetic polymeric dispersant (H) is used, the amount of the synthetic polymeric dispersant (H) contained in the aqueous medium is preferably in the range of 0.0001 to 0.2wt%, more preferably in the range of 0.0002 to 0.15wt%, even more preferably in the range of 0.0005 to 0.1wt% with respect to the weight of the aqueous medium.

[0166]

When the resin (a) and/or the precursor (a0) is dispersed in the aqueous medium, the resin (a) and the precursor (a0) are preferably in the form of liquid or solution. In a case where the resin (a) and the precursor (a0) are solid at room temperatures, the resin (a) and the precursor (a0) may be dispersed at a temperature of the melting point thereof or higher so that they can be dispersed in liquid form, or a solution obtained by dissolving the resin (a) and the precursor (a0) in the above-mentioned solvent (U) may be used.

In a case where the solvent (U) is used, a preferred solvent depends on the kind of resin (a) and precursor (a0) to be used, but the difference in SP value between the resin (a) and the precursor (a0) is preferably 3 or less.

30 [0167]

The viscosities of the resin (a), the precursor (a0), and

solvent solutions thereof are preferably in the range of 10 to 50,000 mPa·s, more preferably in the range of 100 to 30,000 mPa·s, even more preferably in the range of 200 to 20,000 mPa·s, from the viewpoint of particle size uniformity.

5 In this regard, it is to be noted that all viscosities in this specification were measured using a rotor-type viscometer such as a BL-type viscometer, a BM-type viscometer, or a BH-type viscometer (which are manufactured by Tokyo Instruments Co., Ltd.) at a temperature of 25°C.

10 [0168]

A temperature at the time of dispersion is preferably in the range of 0 to 150°C, more preferably in the range of 5 to 98°C, even more preferably in the range of 10 to 60°C. In this regard, it is to be noted that a temperature exceeding 100°C 15 refers to a temperature under pressure.

[0169]

The method for preparing resin particles according to the present invention comprises a step of applying a shear force to an aqueous dispersion (II) with increased viscosity formed 20 by adding a thickener (V) to the dispersant (I) containing the resin particles (A) obtained in such a manner as described above, and a subsequent step of decreasing the viscosity of the aqueous dispersant by adding a viscosity decreasing agent (E).

[0170]

25 As such a thickener (V), water-soluble naturally-occurring polymers and water-soluble semisynthetic polymers, and the like can be used.

30 Examples of the water-soluble naturally-occurring polymers include, but not limited to, polysaccharide-based naturally-occurring polymers (e.g., pullulan, guar gum, locust bean gum, gum Arabic, and starch), and animal-based naturally-occurring polymers (e.g., gelatin and casein).

Examples of the water-soluble semisynthetic polymers include, but not limited to, cellulose-based semisynthetic polymers (e.g., methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, ethylhydroxyethyl cellulose, methylhydroxypropyl cellulose, carboxymethyl cellulose, and sodium carboxymethyl cellulose), starch-based semisynthetic polymers (e.g., soluble starch, carboxymethyl starch, methyl starch, and cationized starch), and alginic acid-based semisynthetic polymers (e.g., alginic acid salts, chitin, and chitosan).

10 [0171]

Among these, cellulose-based semisynthetic polymers are preferable, hydroxyethyl cellulose, acrylic and carboxymethyl cellulose are more preferable, carboxymethyl cellulose is most preferable.

15 [0172]

The amount of the thickener (V) to be added depends on the kind thereof to be used, but is preferably in the range of 0.0001 to 10wt%, more preferably in the range of 0.001 to 5wt%, even more preferably in the range of 0.01 to 2wt% with respect 20 to the weight of the aqueous dispersion (I).

The viscosity of the aqueous dispersion (II) with increased viscosity is preferably in the range of 300 to 100,000 mPa·s, more preferably 1000 to 60000 mPa·s, even more preferably 2000 to 20000 mPa·s. By setting the viscosity of the aqueous 25 dispersion (II) to a value within the above range, it is possible to reduce the time for deforming resin particles by the application of a shear force. In addition, it is also possible to obtain a dispersion in which the deformed resin particles are hard to return to spherical resin particles, that is, it 30 is possible to obtain a dispersion in which deformed resin particles are stable in their shape.

[0173]

A method for deforming the resin particles (A) by the application of a shear force to the aqueous dispersion (II) is not particularly limited, and a well-known method can be used.

An apparatus to be used in applying a shear force is not limited to any specific one as long as it is commercially available as an agitator or a dispersing machine. Examples of trade names of such commercially available dispersing machines include batch-type dispersing machines such as Homogenizer (manufactured by IKA), Polytron (manufactured by KINEMATICA), and TK Auto Homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.), continuous-type dispersing machines such as Ebara Milder (manufactured by Ebara Corporation), TK Filmics and TK Pipeline Homomixer (which are manufactured by Tokushu Kika Kogyo Co., Ltd.), Colloid Mill (manufactured by Shinko Pantec Co., Ltd.), Slusher and Trigonal Wet Mill (which are manufactured by Mitsui Miike Kakoki K.K.), Cavitron (manufactured by EUROTEC Ltd.), and Fine Flow Mill (manufactured by Pacific Machinery & Engineering Co., Ltd.), high-pressure dispersing machines such as Microfluidizer (manufactured by Mizuho Industrial Co., Ltd.), Nanomizer (manufactured by Nanomizer Inc.), and APV Gaulin (manufactured by Gaulin Inc.), membrane dispersing machines such as Membrane Dispersing Machine (manufactured by REICA Co., Ltd.), vibration-type dispersing machines such as Vibromixer (manufactured by REICA CO., Ltd.), and ultrasonic dispersing machines such as Ultrasonic Homogenizer (manufactured by BRANSON).

[0174]

Among these dispersing machines, from the viewpoint of application of a uniform shear force, APV Gaulin, Homogenizer, TK Auto Homomixer, Ebara Milder, TK Filmics, and TK Pipeline Homomixer are preferably used, more preferably TK Auto Homomixer, Ebara Milder, TK Filmics, and TK Pipeline Homomixer, even more

preferably TK Auto Homomixer, TK Filmics, and TK Pipeline Homomixer.

[0175]

A temperature at the time of applying a shear force is
5 not limited to any specific value, but is preferably in the range
of 0 to 60°C, more preferably in the range of 5 to 50°C, even
more preferably in the range of 10 to 40°C, from the viewpoint
of easiness of deformation of resin particles and prevention
of coagulation of resin particles.

10 [0176]

The length of time for the application of a shearing force
depends on the kind of apparatus to be used, and is not particularly
limited. However, from the viewpoint of easiness of deformation
of resin particles and productivity, the length of time for the
15 application of a shear force is preferably in the range of 0.01
second to 6 hours, more preferably in the range of 0.01 second
to 1 hour, even more preferably in the range of 0.01 second to
50 minutes, most preferably in the range of 0.1 second to 20
minutes.

20 [0177]

A shear force to be applied varies depending on the
viscosity of the aqueous dispersion (II), the length of time
for the application of a shear force, and the temperature at
the time of application of a shear force, and can be appropriately
25 determined. However, from the viewpoint of easiness of
deformation of resin particles and easiness of particle diameter
control, a shear force is preferably applied at 10 to 50,000
rpm, more preferably 100 to 20000 rpm, even more preferably 500
to 10000 rpm by, for example, the above-mentioned apparatus for
30 applying a shearing force.

[0178]

The viscosity reducing agent (E) to be used in viscosity

decreasing step after applying a shear force include enzymes [such an enzyme includes α -glycanase (e.g., amylase, dextranase, or pullulanase) and β -glycanase (e.g., cellulase, β -1,3-glucanase, or chitinase)]. These enzymes can be used in combination of two or more of them.

5 [0179]

The amount of (E) to be added is varying depending upon (V), however, from the viewpoint of productivity (e.g., time for decreasing viscosity) and manufacturing costs, the amount 10 of the (E) to be added is preferably in the range of 0.000001 to wt1%, more preferably in the range of 0.000005 to 0.1 wt%, even more preferably in the range of 0.00001 to 0.01 wt% with respect to the weight of the aqueous dispersion (II).

A decreased viscosity of the aqueous dispersion is 15 preferably 200 mPa·s or less, more preferably 100 mPa·s or less, even more preferably 40 mPa·s or less. By setting the decreased viscosity of the aqueous dispersion to a value within the above range, it becomes easy to handle the aqueous dispersion until resin particles (B) are obtained. In addition, it becomes easy 20 to wash the aqueous dispersion in a washing process (which will be described later) carried out as necessary.

[0180]

A temperature at the time of carrying out the viscosity decreasing step is not limited to any specific value, but is 25 preferably in the range of 5 to 40°C, more preferably in the range of 10 to 35°C, even more preferably in the range of 20 to 30°C, from the viewpoint of productivity and a viscosity reduction effect.

[0181]

30 The length of time of the viscosity decreasing step is not limited to any specific value, but is preferably 3 hours or less, more preferably 1.5 hours or less, even more preferably

20 minutes or less, from the viewpoint of productivity.

[0182]

In a case where a solvent has been used at the time of producing the aqueous dispersion (I), the solvent is removed 5 by, for example, heating, decompression, washing with water, or a combination of two or more of them.

[0183]

In a case where the thickener (V), the viscosity reducing agent (E) and the surfactant (S) used adversely affect the 10 physical properties of the resin particles (B) in use, these additives are preferably removed.

An example of a method for removing such additives includes a method, in which the aqueous dispersion is subjected to solid-liquid separation by a centrifuge, a sparkler filter and/or 15 a filter press to obtain resin particles, water is added to the resin particles to again carry out solid-liquid separation with such a means mentioned above, and the latter process is repeatedly carried out.

[0184]

20 The aqueous dispersion of the resin particles (B) obtained in such a manner as described above is subjected to solid-liquid separation (as necessary, solid-liquid separation is repeatedly carried out by adding water or the like), and then the obtained resin particles are dried to remove the aqueous medium, thereby 25 enabling the resin particles (B) of the present invention to be obtained.

[0185]

As a method for removing the aqueous medium, the following 30 methods (1) to (3) and a combination of two or more of them can be employed:

(1) a method in which the aqueous dispersion is dried under reduced pressure or normal atmospheric pressure;

(2) a method in which solid-liquid separation is carried out with a centrifuge, a sparkler filter and/or a filter press, and the resulting solid is dried; and

5 (3) a method in which the aqueous dispersion is freeze-dried (the so-called lyophilization).

[0186]

In the methods (1) and (2), drying can be carried out by well-known machines such as a fluidized-bed type dryer, a vacuum dryer, and an air-circulation dryer.

10 As necessary, the obtained resin particles may be classified with an air classifier or a screen to attain a predetermined particle size distribution.

[0187]

15 The volume average particle diameter (DV) of the resin particles (B) obtained by the preparing method according to the present invention is preferably in the range of 0.1 to 300 μm , more preferably in the range of 0.5 to 250 μm , even more preferably in the range of 1 to 200 μm . By setting the DV to a value within the above range, the SF-1 of the resin particles (B) can lie 20 within the preferred range described above.

In this regard, it is to be noted that the volume average particle diameter can be measured by a laser type particle size analyzer (e.g., "LA-920" which is a product of HORIBA, Ltd. or "Multisizer III" which is a product of Beckman Coulter).

25 [0188]

In a case where it is necessary to improve the powder fluidity of the resin particles (B), the BET specific surface area of the resin particles (B) is preferably in the range of 0.5 to 5.0 m^2/g .

30 In this regard, it is to be noted that the BET specific surface area can be measured with a specific surface area meter (e.g., "QUANTASORB" which is a product of Yuasa Ionics Inc.)

(Measuring gas: He/Kr = 99.9/0.1 vol%, Calibration gas: nitrogen).

[0189]

Similarly, from the viewpoint of powder fluidity, the 5 average of surface roughness (Ra) of the resin particles (B) is preferably in the range of 0.01 to 0.8 μm .

In this regard, it is to be noted that the (Ra) is the 10 arithmetical mean value of the absolute values of the deviation between the roughness curve and the centerline thereof, and can be measured by a scanning probe microscope system (manufactured by, for example, Toyo Corporation).

[0190]

The resin particles (B) according to the present invention 15 can be suitably used as additives for paint, additives for coating materials, powder coatings, additives for cosmetics, resins for slush molding, spacers for use in manufacturing electronic components or devices such as liquid crystal displays, standard particles for electronic measuring instruments, toners for electrophotography, electrostatic recording, and electrostatic 20 printing, hot-melt adhesives, and other molding materials.

[Examples]

The present invention will be further described with 25 reference to the following examples, but the present invention is not limited to these examples. It should be noted that, in the following parts of the specification, all "parts" and "%" are by weight, unless otherwise specified.

<Production Example 1>

In a reaction vessel equipped with a stirring rod and a thermometer, 787 parts of polycaprolactonediol (Mn 2,000) and 30 800 parts of polyether diol (Mn 4,000, EO content 50 wt%, PO content 50 wt%) were placed, and were then subjected to dehydration under reduced pressure at 120°C. The water content

after dehydration was 0.05%. After cooling to 60°C, 55.5 parts of HDI, 65.5 parts of hydrogenated MDI and 0.6 part of dibutyltin dilaurate were added, and then a reaction was carried out for 5 hours at 80°C, to thereby obtain a synthetic polymeric dispersant (1).

Further, 1 part of the synthetic polymeric dispersant (1) was mixed with 200 parts of water with stirring to obtain a milk white dispersant (1).

[0191]

10 <Production Example 2>

In a reaction vessel equipped with a stirring rod and a thermometer, 2,000 parts of polycaprolactonediol having a hydroxyl value of 56 ("PLACCEL L220 AL" manufactured by Daicel Chemical Industries, Ltd.) was placed, and was then subjected to dehydration for 1 hour under heating to 110°C at a reduced pressure of 3 mmHg. Then, 457 parts of IPDI was added, and a reaction was carried out for 10 hours at 110°C, to thereby obtain an isocyanate-terminated urethane prepolymer (1). The NCO content of the urethane prepolymer (1) was 3.6%.

20 [0192]

<Production Example 3>

In a reaction vessel equipped with a stirring rod and a thermometer, 50 parts of ethylenediamine and 50 parts of MIBK were placed, and then a reaction was carried out for 5 hours at 50°C, to thereby obtain a ketimine compound [curing agent 1].

[0193]

<Example 1>

In a reaction vessel equipped with a stirring rod and a thermometer, 48 parts of styrenated phenol-EO adduct ("ELEMINOL HB-12" manufactured by Sanyo Chemical Industries Ltd.) and 241 parts of bisphenol A diglycidylether ("Epikote 828" manufactured

by Yuka Shell) were placed, and then they were homogeneously dissolved.

Next, water was dropped into the reaction vessel under stirring. At the time when the amount of water dropped had 5 reached to 31 parts, the content of the reaction vessel was emulsified so that the color thereof became milk white. 236 parts of water was further added, to obtain a dispersion.

After the obtained dispersion was heated to 73°C, a mixed solution of 20 parts of ethylenediamine and 446 parts of water 10 was dropped into the dispersion over 2 hours, with the internal temperature of the reaction vessel being maintained at 73°C.

After the completion of dropping, a reaction was carried out for 4 hours at 73°C, and then a reaction product was matured for 4 hours at 90°C, to thereby obtain an aqueous dispersion 15 (X1-1).

[0194]

To 100 parts of the (X1-1), 3 parts of carboxymethyl cellulose ("CELLOGEN HH" manufactured by Daiichi Kogyo Seiyaku Co., Ltd.) was added, and then they were stirred with a Homogenizer 20 (manufactured by IKA) at 1,000 rpm for 10 minutes at 25°C to obtain a dispersion (X1-2). The viscosity of the dispersion (X1-2) was 3,300 mPa·s. Further, 0.02 part of amylase was added, and the resulting mixture was stirred for 3 minutes at 25°C to obtain a dispersion (X1-3). The viscosity of the dispersion 25 (X1-3) was 50 mPa·s.

103 parts of the (X1-3) was centrifuged. After addition of 50 parts of water, solid-liquid separation was carried out by centrifugation, and this process was repeated twice. After drying for 1 hour at 35°C, resin particles (Y-1) were obtained. 30 The physical properties of the (Y-1) are shown in Table 1.

[0195]

<Example 2>

In a beaker, 140 parts of the urethane prepolymer (1) and 5 parts of the curing agent (1) were mixed, and then 265 parts of the dispersion (1) was added thereto. Then, they were mixed with an Ultra-disperzer (manufactured by Yamato Scientific Co., Ltd.) at 9,000 rpm for 1 minute at 25°C, to obtain an aqueous dispersion (X2-1).

To 100 parts of the (X2-1), 1 part of carboxymethyl cellulose ("CELLOGEN F-3H" manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), and then they were stirred for 10 minutes at 25°C, to obtain a dispersion (X2-2). The viscosity of the (X2-2) was 5,600 mPa·s. The (X2-2) was stirred with a TK Homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.) at 3,000 rpm for 10 minutes at 25°C.

Further, 0.01 part of cellulase ("Cellulase AP3" manufactured by Amano Enzyme Inc.) was added, and the resulting mixture was stirred for 5 minutes at 25°C, to obtain a dispersion (X2-3). The viscosity of the (X2-3) was 20 mPa·s.

100 parts of the (X2-3) was centrifuged. After addition of 40 parts of water, solid-liquid separation was carried out by centrifugation, and this process was repeated twice. After drying for 1 hour at 35°C, resin particles (Y-2) were obtained. The physical properties of the (Y-2) are shown in Table 1.

[0196]

<Example 3>

In a beaker, 140 parts of the [prepolymer 1], 5 parts of the [curing agent 1] and 50 parts of ethyl acetate were mixed, and then 465 parts of water and 3 parts of dodecylnaphthalenesulfonic acid sodium salt were added. Thereafter, they were mixed with a TK Homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.) for 1 minute at 12,000 rpm at 25°C, to thereby obtain an aqueous dispersion (X3-1).

To 100 parts of the aqueous dispersion (X3-1), 2 parts

of carboxymethyl cellulose ("CELLOGEN HH" manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), and the resulting mixture was stirred with a TK Homomixer for 8 minutes at 2,500 rpm at 25°C, to thereby obtain a dispersion (X3-2). The viscosity of the (X3-2) was 4,900 mPa·s. Further, 0.05 part of cellulase ("Celluclast" manufactured by Novozymes Japan Ltd.) was added, and then the resulting mixture was stirred for 5 minutes at 25°C, to thereby obtain an (X3-3). The viscosity of the (X3-3) was 40 mPa·s.

10 100 parts of (X3-3) was centrifuged. After addition of 60 parts of water, solid-liquid separation was carried out by centrifugation, and this process was repeated twice. After drying for 1 hour at 35°C, resin particles (Y-3) were obtained. The physical properties of the resin particles (Y-3) are shown
15 in Table 1.

[0197]

<Comparative Example 1>

20 In a beaker, 150 parts of the urethane prepolymer (1) and 6 parts of the curing agent (1) were mixed, and then 250 parts of the dispersion (1) was added. Then, they were stirred with an Ultra-disperser (manufactured by Yamato Scientific Co., Ltd.) at 9,000 rpm for 20 minutes at 25°C, to obtain an aqueous dispersion (HX1-1).

25 100 parts of the (HX1-1) was centrifuged. After addition of 40 parts of water, solid-liquid separation was carried out by centrifugation, and this process was repeated twice. After drying for 1 hour at 35°C, resin particles (HY-1) were obtained. The physical properties of the (HY-1) are shown in Table 1.

[0198]

30 <Comparative Example 2>

In a beaker, 150 parts of the prepolymer (1), 6 parts of the curing agent (1), and 40 parts of ethyl acetate were mixed,

and then 457 parts of the dispersion (1) was added. Then, they were stirred with a TK Homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.) at 12,000 rpm for 20 minute at 25°C, to obtain an aqueous dispersion (HX2-1).

5 100 parts of the (HX2-1) was centrifuged. After addition of 40 parts of water, solid-liquid separation was carried out by centrifugation, and this process was repeated twice. After drying for 1 hour at 35°C, resin particles (HY-2) were obtained. The physical properties of the (HY-2) are shown in Table 1.

10 [0199]

[Table 1]

	Examples			Comparative Exps.	
	1	2	3	1	2
Resin particles	(Y-1)	(Y-2)	(Y-3)	(HY-1)	(HY-2)
Shape factor SF-1	171	185	189	116	118
Volume average particle diameter of resin particles (μm)	89	7.3	6.4	7.4	7.1
Average of surface roughness	0.55	0.19	0.22	0.63	0.21
BET specific surface area (m ² /g)	2.3	3.5	3.9	2.4	4.1

[0200]

[Effects of the invention]

15 1. According to the preparing method of resin particles of the present invention, it is possible to reduce the time for deforming resin particles. Further, the deformed resin particles have excellent shape stability. Furthermore, since the preparing method of the present invention is carried out in an aqueous medium, it is very safe as compared with conventional methods.

20 2. The resin particles obtained by the preparing method of the present invention are not spherical particles (but are spindle or rod-shaped particles) so that they can have a very

large surface area. Further, the resin particles of the present invention have a uniform particle diameter and excellent powder fluidity and storage stability.

Therefore, the resin particles of the present invention
5 provide the following effects.

Since the resin particles of the present invention are spindle or rod-shaped particles (that is, the SF-1 thereof ranges from 130 to 300), they show significant thixotropy when dispersed in a solvent or an aqueous medium. For this reason, the resin
10 particles of the present invention can be suitably used as a fluidity improver for paint or coating materials.

Further, the alignment of the resin particles in the formation of a coating layer is uniform in the direction of longer diameter of the resin particles. Therefore, the resin particles
15 of the present invention provide the effect of preventing blister from occurring in forming a coating layer and the effect of improving luster or a gloss of a coating.

Furthermore, in a case where the resin particles of the present invention are blended in cosmetics such as lipstick and
20 foundation, they provide smooth feeling when such cosmetics are applied to the skin.

Moreover, in a case where the resin particles of the present invention are used as a toner, cleaning of the toner with a cleaning blade is facilitated.

[Document Name] ABSTRACT

[Abstract]

[Problem] This invention is to provide a non-spherical (e.g., a spindle- or rod-shaped resin particle) resin particle with 5 large surface area, and a method for preparing such resin particles.

[Means to solve the problem] A method for preparing resin particles, comprising the steps of: applying a shear force to an aqueous dispersion (II) with increased viscosity formed by 10 adding a thickener (V) to an aqueous dispersion (I) containing resin particles (A); and a subsequent step of decreasing the viscosity of the aqueous dispersion by adding a viscosity decreasing agent (E), and the resin particles (B) obtained by the method.

15 [Selected figure] none